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ON THE CONSTITUTION OF THE SALTS OF IMIDO-ETHERS AND OTHER CARBIMIDE DERIVATIVES.

BY JULIUS STIEGLITZ.

Substances containing a carbimide group (C = NR) are usually found to unite readily with acids, especially with hydrochloric acid. The addition-products in nearly every case have the appearance of salts, and in most cases their properties. From the first discovery of these compounds the tendency has been to ascribe the formation of such salts to the presence of the nitrogen atom alone, the addition-products being considered derivatives of ammonium salts $C=N^{V}RHCl$ simply because they are salts. In one or two cases it has already been shown that the hydrogen chloride is really taken up at the double bond of the carbimide group or by the carbon atom alone. Thus, the addition-products of the isocyanates, OC : NR, and hydrogen chloride, the urea chlorides, have been shown by Gattermann[1] to be chlorformamides, ClCONHR. The addition-products of hydrocyanic acid, C : NH, and fulminic acid, C : NOH, with hydrogen chloride have in general the constitution of acid imide chlorides, *e. g.*, ClCH(: NOH),[2] the chlorine atom going to the carbon. These very hydrochlorides, however, for which the ammonium form of constitu-

[1] Ann. Chem. (Liebig), **244**, 29.
[2] Nef : *Ibid.*, **287**, 342, etc.; **280**, 303.

tion has been rejected are not salts of bases but are rather acid chlorides. In the case of the salts of true carbimide bases like the imido-ethers, RC(:NR)OR, the amidines, RC(:NR)NHR, the pyridines, quinolines, etc., it has been assumed without further experimental evidence that they must be ammonium salts with quinquivalent nitrogen [$C(:N^{V}RHCl)$]. The alternative constitution [CCl(NHR)], has not been considered for such derivatives, probably for the reason that the grouping C—Cl has always been held to be necessarily either an *acid chloride* grouping as in RCOCl, RC(NR)Cl, etc., or a hydrochloride acid *ester* grouping as in the alkyl chlorides. In terms of the theory of ionization chemists have accepted the positive ammonium ions R_4N^+, whose existence is beyond any doubt, but the possibility of the existence of positive carbon ions R_3C^+ has as yet hardly been considered or, when considered, rejected off-hand.[1] The very fact of ionization of chlorides has been used to disprove the possibility of chlorine being attached to carbon.[1] It is true the behavior of simple carbon derivatives undoubtedly containing the group C—Cl, the alkyl halides, etc., so far as studied, seems entirely in accord with such a course, although minimal ionization into R_3C^+ and Cl^- in such cases has not been disproved, and even seems probable.[2] But should this not prove to be the case, it would not dispose of the possibility that under certain favorable conditions we can have positive carbon ions, salts of carbon bases which are capable of stronger electrolytic dissociation. We have sulphur, phosphorus, iodine bases, etc., why not carbon bases? It has been chiefly with the object of getting further experimental evidence on this subject, either for or against the possibility suggested, that a series of studies has been undertaken and partly completed in the last two years by my students in this laboratory. A favorable starting-point seemed to be the carbimide bases mentioned above. The behavior of the hydrochlorides of imido-ethers, particularly the ease with which they break down at comparatively low temperatures into alkyl chloride and acid amide led me to suspect that they

[1] Miolati: Ber. d. chem. Ges., **26**, 1788; **28**, 1696; Tortelli: *Ibid*, **28**, 1702.
[2] *Vide e. g.*, Ostwald: Lehrb. allgem. Chem., Vol. II, 788.

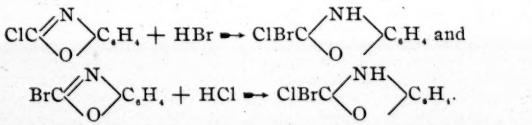
really have the constitution $RC(NH_2)(Cl)(OC_2H_5)$. Facts observed in the course of an investigation in collaboration with Dr. Lengfeld on the action of phosphorus pentachloride on urethanes[1] led us to the same conclusion, and induced us to test it by comparing the hydrobromide of chlorformphenylimido-ether with the hydrochloride of bromformphenylimido-ether.[2] The results pointed to the formation of the same salts in both cases thus :

$ClC(:NC_6H_5)OC_2H_5 + HBr \rightarrow ClBrC(NHC_6H_5)(OC_2H_5)$ and $BrC(:NC_6H_5)OC_2H_5 + HCl \rightarrow ClBrC(NHC_6H_5)(OC_2H_5)$.

This salt could not be isolated on account of its extreme instability. It decomposed even at $-15°$. But from the fact that the same decomposition-products (chiefly ethyl bromide and chlorformanilide) were obtained in both reactions, the intermediate formation of the same addition-product was inferred. That such a salt is capable of existence under more favorable conditions of the molecule was demonstrated by the preparation and analysis of the hydrochloride of chlorformphenylimidophenyl ester :

$ClC(:NC_6H_5)OC_6H_5 + HCl \rightarrow Cl_2C(NHC_6H_5)(OC_6H_5)$.

The subject seemed, however, too important to rely entirely on the formation of an intermediate product which was not isolated in the critical test. For this reason, Mr. H. N. McCoy at my request has tested the question further by comparing the hydrobromide of chlorformphenyleneimido-ether with the hydrochloride of bromformphenyleneimido-ether. As described in Mr. McCoy's paper (see next article) these salts were *isolated* and proved *identical*. They must therefore be formed according to :



[1] Lengfeld and Stieglitz : This JOURNAL, **16**, 76. [2] This JOURNAL, **17**, 98.

That such addition-products are true salts of bases, however weak the bases are, was proved by their solubility in water in presence of an excess of acid, and by the preparation and analysis of a chlorplatinate and a nitrate corresponding to the hydrochloride of chlorformphenyleneimido-ether. Therefore, unless rearrangements in the molecule, extremely improbable under the conditions of the experiments, have taken place, the constitution of the salts of these imido-ethers is that of carbon bases and not of ammonium bases. These facts, in connection with the results of Dr. Lengfeld and myself, and the analogous behavior of all imido-ethers, warrant the conclusion that the salts of all imido-ethers have the constitution RC X (NHR)(OR). This conclusion is being still further tested[1] in as many different ways as seem possible. So far all direct experimental evidence points one way.

In another case the possibility of the existence of salts of carbon bases of the nature indicated has been investigated. According to Mr. McCoy's results (see next article) which confirm the preliminary conclusions of Lengfeld and myself,[2] the constitution of the hydrochloride of carbodiphenylimide, $C(:NC_6H_5)_2$, is expressed by the formula $(C_6H_5NH)(C_6H_5N:)CCl$. And Mr. F. B. Dains[3] working under my direction in this laboratory has shown that the salt-forming power of carbodiphenylimide is not confined to hydrochloric acid. He has prepared and analyzed a number of chlorplatinates of carbodialphylimides, whose composition, $[(RNH)(RN:)C]_2PtCl_6$, corresponds to that of their chlorides. Undoubtedly the chlorides have also some resemblance to acid chlorides, being rapidly decomposed by water and reacting readily with sodium alcoholate, but the dual character

[1] One method is indicated in a preliminary report by Mr. Ransom (Ber. d. chem. Ges., **31**, 1055), who will report later in this JOURNAL. Another method that Mr. Wm. McCracken will use is the attempt to prepare two isomeric dichlorides $C_6H_4\langle^{O}_{NCH_3}\rangle CCl_2$ and $C_6H_4\langle^{O}_{N}\rangle CCl$ and study the salt characteristics of a body of the former constitution.

[2] This JOURNAL, **17**, 107; Stieglitz: Ber. d. chem. Ges., **28**, 573.

[3] *Vide* a paper by Mr. Dains which will appear in one of the next numbers of the Journal of the American Chemical Society.

repeats only in an organic compound what is quite common in inorganic chlorides.[1]

Mr. Dains[2] has also made an exhaustive study of the chemical behavior of the aromatic isourea ethers, for instance ethylisocarbanilide,[3] $(C_6H_5NH)(C_6H_5N:)COC_2H_5$. His work has led to very interesting and instructive results bearing both on the constitution of the salts of imido ethers and on their general chemical behavior. Ethyl isocarbanilide, although it contains both the basic phenylimido-ether group $-C(:NC_6H_5)(OC_2H_5)$ and the second basic anilido group $C_6H_5NH-$is a *mono-acid* base. It unites with 1 molecule of hydrochloric acid giving $(C_6H_5NH)C(:NC_6H_5)(OC_2H_5)$. HCl, and its chlorplatinate has the composition $[(C_6H_5NH)C(:NC_6H_5)OC_2H_5]_2H_2PtCl_6$. This agrees best with the constitution $(C_6H_5NH)_2CCl(OC_2H_5)$ for the hydrochloride. This view of the constitution is strongly supported by the behavior of the urea ether towards aqueous hydrochloric acid. The ordinary imido-ethers heretofore known, such as ethyl imidobenzoate, ethyl phenylimidoformate, etc., show a reaction which has been considered typical for the imido-ethers: with dilute aqueous acids they are rapidly saponified even in the cold into amines and acid esters according to:

$$RC(:NR)OR + HCl + H_2O \rightarrow RCOOR + (NH_2R)Cl.$$

Alkyl isocarbanilides are very much more stable; they are not decomposed completely even after standing weeks in cold dilute acids, and when they are decomposed by dilute hydrochloric acid, they invariably react as follows:

$$(C_6H_5NH)_2CCl(OC_2H_5) \rightarrow ClC_2H_5 + (C_6H_5NH)_2CO,$$

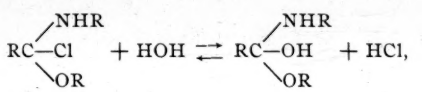
yielding ethyl chloride and a carbanilide, and not aniline and a urethane! Considering that such a striking change of reaction takes place in going simply from weaker bases to much stronger ones of the same class of compounds, and that the

[1] An interesting reaction of acetic acid on carbodialphylimides, investigated by Mr. Dains, supports the constitution given above to the hydrochloride of carbodiphenylimide; the evidence will be fully discussed by Mr. Dains in his paper in the Journal of the American Chemical Society. Compounds $(R_2N)(RN:)CCl$ will also be prepared to obtain further light on the question.

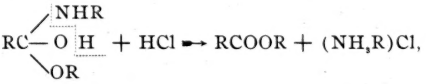
[2] *Loc. cit.*

[3] Lengfeld and Stieglitz: Ber. d. chem. Ges., **27**, 926; This JOURNAL, **17**, 984; and Stieglitz: Ber. d. chem. Ges., **28**, 573.

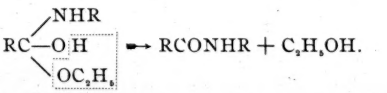
difference in behavior is only shown towards aqueous acid—all of the compounds belonging to the class of imido-ethers give alkyl chlorides and acid amides with anhydrous hydrogen chloride—the conclusion is inevitable that the change in behavior must be due to the different hydrolytic action of water on the chlorides. As among inorganic chlorides we have gradual changes in action towards water on going, *e. g.*, from phosphorus pentachloride through aluminium and magnesium chloride to sodium chloride, there can be no doubt that the hydrochlorides of imido-ethers with weaker basic functions must be hydrolyzed more or less in aqueous solution, and that the stronger the basicity of the imido-ether the smaller the degree of hydrolysis of the chloride. Ordinary imido-ethers like benzimidoethyl ether, formphenylimidoethyl ether, etc., being much weaker bases than the urea ethers, their hydrochlorides must be more or less hydrolyzed in aqueous solution:[1]



and the free imido ether base formed can readily break down into an amine and an acid ester according to



or, under certain conditions, into alcohol and an acid amide:[2]



The urea ethers being much stronger bases, their hydrochlorides are found to be much more stable in aqueous solution,

[1] The hydrochloride of benzimidoethyl ether that had stood for a number of months over solid potassic hydrate in a desiccator gave a solution in water which immediately reacted decidedly acid towards litmus. A solution of the hydrochloride of metanitrobenzimidoethyl ether showed a very strong acid reaction.

[2] Comstock and Wheeler: This JOURNAL, **13**, 522.

and, when they do decompose, they slowly give the decomposition-products of the hydrochlorides themselves :

$$(C_6H_5NH)_2C\begin{matrix}\diagup Cl\\ \diagdown O\,C_2H_5\end{matrix} \longrightarrow (C_6H_5NH)_2CO + ClC_2H_5.$$

No other conception of the constitution of the hydrochlorides of imido-ethers and urea ethers explains so simply their different behavior towards aqueous acids.[1] This interpretation of the constitution of the hydrochlorides of the isocarbanilides is further supported by another important discovery concerning the chemical behavior of the isocarbanilides. A second reaction of the imido-ethers, which hitherto had to be regarded as typical is that with amines, yielding amidines with great ease. In the analogous action of amines on acid esters it is now commonly assumed that the reaction takes place with the formation of an intermediate product[2] as follows :

$$RCOOR + H_2NR \rightleftarrows RC\begin{matrix}\diagup NHR\\ -OH\\ \diagdown OR\end{matrix} \rightleftarrows RCONHR + HOR,$$

and there is every reason to suppose that in the action of amines on imido ethers the same kind of intermediate addition product is formed :[3]

$$RC(:NR)OR + R'NH_2 \longrightarrow RC(NHR)(NHR')OR \longrightarrow RC(NHR)(:NR') + HOR.$$

It is worth noting that the imido-ethers react the more rapidly and easily in this direction, the more negative their molecule

[1] The characteristic difference between the imido-ethers and the urea ethers recalls the fact that amidines like *s*-benzdiphenylamidine, $C_6H_5C(:NC_6H_5)NHC_6H_5$, are much more readily saponified to anilines and benzanilides than the corresponding guanidines are (Wallach : Ann. Chem. (Liebig), **184**, 85); *e. g.*, triphenylguanidine, $(C_6H_5NH)C(:NC_6H_5)NHC_6H_5$. The explanation given for the former case fits admirably the amidines as well.

[2] *Vide, e. g.*, Lossen : Ann. Chem. (Liebig), **252**, 103.

[3] This is made practically certain by the fact that besides an amidine very frequently a new imido-ether is formed according to :

$$RC\begin{matrix}=NR\\ \diagdown OR\end{matrix} + H_2NR' \longrightarrow RC\begin{matrix}\diagup NHR\\ -NHR'\\ \diagdown OR\end{matrix} \longrightarrow RC\begin{matrix}=NR'\\ \diagdown OR\end{matrix} + H_2NR,$$

(Lossen : Ann. Chem. (Liebig), **265**, 138).

is. Thus phenylimidoformic ethers,[1] succinimido-ether,[2] etc., give amidines especially readily. Naturally, the addition of the positive amine groups is facilitated by the negative condition of the amido-ether. Now, where the imido-ether is very strongly positive, as is ethyl isocarbanilide, this typical imido-ether reaction is almost entirely suppressed. Under all ordinary conditions aniline and ammonia do not react at all with ethyl isocarbanilide; only by prolonged heating with aniline at 200° in a sealed tube was a small amount of triphenylguanidine obtained.[3] It seems plausible that such a positive urea ether should take up and hold hydrochloric acid so firmly as described above and that it should resist the addition of aniline at the same place in the molecule, an addition which, as shown, seems necessary to make it react at all with aniline. In this way we have the same simple cause for both the abnormal (new) characteristics of the isocarbanilides in which they differ so strikingly from ordinary imido-ethers. The intimate connection of the two was shown by Mr. Dains by preparing a urea ether with more negative radicals, ethyl isodicarbethoxylurea,

$$(C_2H_5O)C(:NCOOC_2H_5)(NHCOOC_2H_5).$$

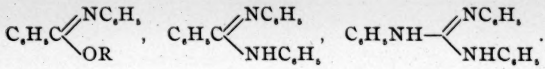
This compound is rapidly decomposed by hydrochloric acid and it also reacts readily with ammonia, forming dicarbethoxylguanidine $(NH_2)C(:NCOOC_2H_5)(NHCOOC_2H_5)$.

Further evidence on the constitution of the hydrochloride of ethyl isocarbanilide can be drawn from its behavior towards benzoyl chloride. This is fully discussed by Mr. Dains in his paper on the subject.

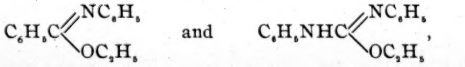
All the experimental data gathered in this laboratory on the subject of the constitution of the hydrochlorides of imido-ethers and similar carbimide bases point, therefore, in the same direction, that these salts are not ammonium salts but are formed by the addition of hydrogen chloride to the double bond of the carbimide group, C : NR. A glance at the literature brings strong indications confirming such a view, not only for imido-ethers but closely allied imido derivatives. It

[1] Comstock and Kleeberg : This JOURNAL, 12, 498.
[2] Comstock and Wheeler : *Loc. cit.*
[3] Dains : *Loc. cit.*

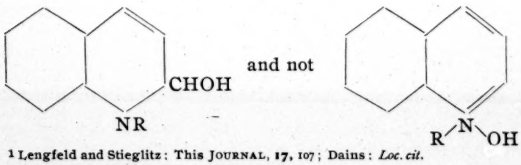
is a significant fact that phenylimidobenzoic ether, *s*-diphenylbenzamidine, and triphenylguanidine,



all form salts with one molecule of acid in spite of the increasing number of amine groups. They all have one double bond ($C : NC_6H_5$) in common—nothing else. In the same way phenylimidobenzoic ether and ethyl isocarbanilide (anilidophenylimidoformic ether),

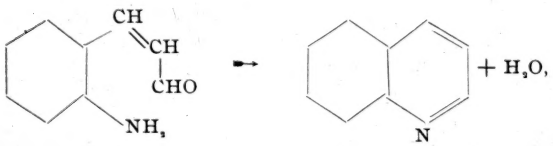


form salts with only one molecule of acid. On the other hand, carbodiphenylimide, carboditolylimide, etc, $C_6H_5N = C=NC_6H_5$, etc., with two double bonds, take up two molecules of hydrogen chloride[1] with such avidity that it was a matter of greatest experimental difficulty to isolate a monochloride ;[1] and carbanilide $(C_6H_5NH)_2CO$, with no carbimide double bond but two anilido groups does not form any hydrochloride ! These facts so strongly corroborate direct experimental evidence discovered so far, that the work will be continued along analogous lines on the constitution of the salts of the amidines, thioimido-ethers, etc., as well as the imido-ethers. It will include an investigation of the constitution of the salts of pyridine and quinoline. The hydroxides obtained from alkylquinolinium salts are now considered, according to the investigations of Roser,[2] Decker,[3] etc., to have the constitution

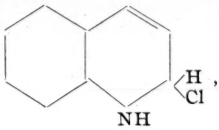


[1] Lengfeld and Stieglitz : This JOURNAL, **17**, 107 ; Dains : *Loc. cit.*
[2] Ann. Chem. (Liebig), **272**, 221 ; **282**, 373.
[3] Ber. d. chem. Ges., **25**, 3326 ; J. prakt. Chem., **45**, 161; **47**, 222.

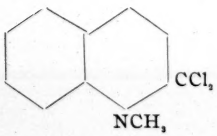
an ammonium hydroxide. The salts, however, are still universally supposed to be ammonium salts, even by Roser and Decker, while no experimental evidence has been brought to bear on the subject. Quinoline is a phenylimide derivative (phenyleneimidoacrolein) as is shown by its synthesis (from *o*-amidocinnamic aldehyde)



and constitution, and it seems possible that its salts should have the constitution



corresponding to that developed for phenylimido-esters, and to that of the hydroxides obtained from the quinoline salts. The problem of the constitution of the pyridine and quinoline salts will be investigated in the near future, by comparing the hydrochloride of α-bromquinoline and the hydrobromide of α-chlorquinoline as well as by an attempt to prepare isomeric dichlorides,



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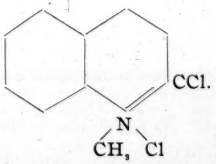


The work completed and outlined deals entirely with the constitution of salts of carb(phenyl)imide derivatives. The foothold obtained in working on the imido-ethers and carbodiphenylimide seems to indicate that accumulation of positive imido groups attached to a carbon atom transfers their positive effect to make the carbon radical a positive ion. It may be added that on account of the importance of the question of the existence of carbon ions R_3C^+ and, in view of the behavior of ordinary compounds containing the group C—Cl, a great deal of hesitation is felt in accepting any results as final before more evidence is collected; but, so far, the experimental results have been surprisingly unanimous in support of the views expressed. Should they continue to be so, the ultimate aim will be to find carbon bases free from nitrogen, and it is hoped that such will be found in some tertiary alcohols.

CHICAGO, October, 1898.

ON THE HYDROCHLORIDES OF CARBO-PHENYLIMIDO DERIVATIVES.

HERBERT N. MCCOY.

Many bodies containing the carbo-phenylimido group, $C{=}NC_6H_5$, combine readily with acids, particularly the halogen acids, to form salt-like compounds. In the preceding paper by Prof. Stieglitz, it is shown that it is a question of considerable importance to determine experimentally whether, in any given class of such compounds, the acid is taken up by the nitrogen atom, forming ammonium derivatives; or is absorbed by the double bond between carbon and nitrogen, the halogen going to the carbon and the hydrogen to the nitrogen atoms, while the valence of the nitrogen remains unchanged.

The work, an account of which is given in the present paper, was undertaken at the suggestion and under the direction of Dr. Stieglitz, with the object of investigating two such cases. The first part of the paper deals with the experiments on the constitution of the hydrochlorides, etc., of phenylimido acid esters, RC(: NR)OR; the second part comprises a study

of the constitution of the addition-products of hydrogen chloride and carbodiphenylimide, $C(:NC_6H_5)_2$.

PART I.

On the Hydrochlorides of Phenylimido Acid Esters.

The imido esters, $R''C(:NR)OR'$, form crystalline salts with acids[1], particularly with the halogen acids. These salts have been considered by their discoverer, Pinner, and by others, to have the general constitution, (I) $R''C(OR')(:N^{V}RHX)$, the nitrogen atom being quinquivalent.

In 1894 Lengfeld and Stieglitz[2] in the course of a study of the action of phosphorus pentachloride on phenylurethane, were led to examine the question whether the salts of the imido esters might not have the constitution represented by the formula, (II) $R''C(\overset{H}{NR})(X)(OR')$, the hydrogen haloid having been added to the double bond. The results of their investigation of the action of hydrogen bromide on ethyl phenylimidochlorformate and of hydrogen chloride on ethyl phenylimidobromformate indicated that in both cases the same addition-product or salt is formed. This is only possible if formula II represents the true constitution of these salts.

$$Cl-C(=NC_6H_5)(OC_2H_5) + HBr \rightarrow Cl\,C(\overset{H}{N-C_6H_5})(Br)(OC_2H_5) \qquad (A);$$

$$Br-C(=NC_6H_5)(OC_2H_5) + HCl \rightarrow Br\,C(NC_6H_5)(Cl)(OC_2H_5) \qquad (B).$$

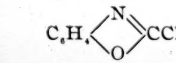
The products A and B should be identical. The identity

[1] Pinner: Ber. d. chem. Ges., **10**, **11**, **16**, **17**, etc.

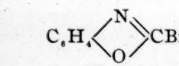
[2] This JOURNAL; **16**, 70; **17**, 98.

of these salts could not be proved by isolating them, as they decompose below —15°. However, as A and B gave the same *decomposition-products* (in both cases chiefly ethyl bromide and chlorformanilide) the only simple explanation is to be found in the assumption that the above identical addition-compounds are the intermediate products of the reaction.

The fact that the salts mentioned were too unstable to be isolated and compared directly made it desirable to obtain and compare more stable salts of the same class of compounds. With this object in view, I have investigated the salts formed by the action of acids on chlormethenyl-*o*-aminophenol[1],



—and on brommethenyl-*o*-aminophenol,



compounds which are imido-esters of the same type as the compound $R''C(:NC_6H_5)OR$.

A great deal of work was necessary in order to find suitable methods for preparing the substances.

Chlormethenylaminophenol (carbonylaminophenol chloride) had been prepared by Seidel[2] by the action of phosphorus pentachloride on *o*-thiocarbamidophenol; but the yield was poor, and the method failed entirely, in attempting to prepare the brommethenylaminophenol, necessary for the investigation, by the action of phosphorus pentabromide on the thio-compound. After trying a number of methods described below, it was found that these two substances can be prepared very readily and with excellent yields by the action of dry chlorine or bromine on the thio-compound suspended in dry chloroform, and subsequent treatment with water, thus :

$$O.C_6H_4.NH.CS + 2Cl_2 \rightarrow O.C_6H_4.N:CCl + HCl + SCl_2.$$

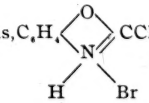
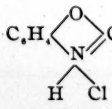
On account of the ring structure of these imido esters the hydrogen-haloid addition-products should show no tendency to split off alphyl haloid, corresponding to a loss of ethyl haloid in the case of the bodies studied by Lengfeld and Stieglitz;

[1] Concerning the nomenclature *vide* Ladenburg: Ber. d. chem. Ges., **10**, 1124.
[2] J. prakt. Chem., [2], **42**, 454.

in fact, the addition-products were found to be capable of isolation.

The hydrochloride, obtained by the action of dry hydrogen chloride on a ligroin solution of chlormethenylaminophenol is a white crystalline salt-like body, which is stable in an atmosphere of hydrogen chloride at the ordinary temperature, and decomposes, with loss of hydrogen chloride, at 57°. Water dissociates the salt at once into hydrochloric acid and chlormethenylaminophenol; but in concentrated hydrochloric acid chlormethenylaminophenol, which is an oil insoluble in water, is very readily soluble and separates as the unchanged oil, on diluting with water; thus showing that the oil is a true, though weak base.

The hydrobromide of chlormethenylaminophenol, obtained by the action of carefully dried hydrogen bromide on a solution of the chlorine compound in dry ligroin, was found to be a fairly stable substance, decomposing, when dry, only above 155°.

The hydrochloride of the corresponding brommethenylaminophenol, prepared from the latter by the addition of dry hydrogen chloride, had the same composition, melting-point and other properties as the above hydrobromide of chlormethenylaminophenol. The salts are decomposed by water, *both giving hydrobromic acid* and *chlormethenylaminophenol*. The two bodies appear to be identical in every respect. This can only be the case when both bodies are represented by the formula, $O{-}C_6H_4{-}NH{-}CClBr$; while according to the old conception the bodies would have the formulas,  and  , and they would evidently have different properties. Besides those mentioned, other salts of these substances were prepared and analyzed: the nitrate, and the

chlorplatinate of chlormethenylaminophenol, and the hydrobromide of brommethenylaminophenol, thus establishing their salt-like nature beyond a doubt.

The results of the investigation of the salts of chlor- and of brommethenylaminophenol are therefore in complete accord with the views of Lengfeld and Stieglitz[1] on the constitution of the salts of the amido ethers. Carbo-phenylamido derivatives are weak bases and the hydrogen-haloid addition-products are true salts, in which *the halogen is bound to carbon* and the hydrogen to nitrogen; and they may in general be represented by the formula, $R''C\begin{cases}NHR\\-X.\\OR'\end{cases}$

In connection with the investigation of the salts of chlormethenylaminophenol, the opportunity was used to study the action of phosphorus pentachloride on carbonylaminophenol somewhat more fully than had been done by previous investigators.[2] It was decided to determine whether carbonylaminophenol or certain of its derivatives would react with phosphorus pentachloride according to:

$$\underset{\llcorner\!\!_\!\!_\!\!_

EXPERIMENTAL PART.

The Action of Potassium Hypobromite on Salicylic Amide.

In order to prepare the carbonylaminophenol needed, a new method was tried, starting from salicylic amide, and based on the molecular rearrangement which bromamides show when treated with alkalies or alcoholic sodium methylate[1].

The preparation of salicylic amide by heating the methyl ester with concentrated aqueous ammonia[2] gives good results only when the heating is continued several days at 100°. By heating, in a sealed tube, one part of the ester with two parts of 36 per cent. ammonia and one and one-half parts of pure methyl alcohol for six hours at 100°, very good yields of the amide were obtained. The alcohol greatly accelerates the action by dissolving both the ester and the ammonia. From theoretical considerations, it is evident that the ultimate yield of amide must be somewhat diminished by the use of alcohol; but the cheapness of the material, the greater purity of the product, and the saving of time make the new method preferable.

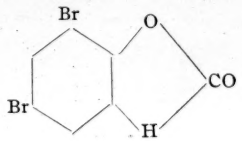
To prepare salicylic bromamide the method of Hoogewerff and Van Dorp[3] was adopted. To an alkaline solution of potassium hypobromite, made from one molecule of bromine and four molecules of caustic potash in 10 per cent. solution, was added one molecule (5 grams) of dry salicylic amide in small portions, the temperature of the solution being kept below 5°. The amide dissolved forming a clear solution, which, treated with cold dilute acetic acid, gave a nearly white precipitate. This was not the expected salicylic bromamide, since, when treated with potassium iodide and hydrochloric acid, no iodine was liberated. Further examination showed the precipitate to consist of a body containing bromine mixed with much unchanged salicylic amide. A second experiment, with two molecules of bromine and six of caustic potash to one of the amide, gave a similar product which, however, contained less unchanged amide. Finally, one molecule of salicylic amide

[1] Hofmann; Ber. d. chem. Ges., **15**, 762; Hoogewerff and Van Dorp: Recueil trav. chim., **9**, 33; **10**, 4; Lengfeld and Stieglitz: This JOURNAL, **15**, 215, 504; **16**, 370.

[2] Spilker: Ber. d. chem. Ges., **22**, 2768.

[3] Rec. trav. Chim., **4**, 373.

(5 grams) was added to the alkaline hypobromite solution, obtained from three molecules of bromine (17.8 grams) and eight molecules of caustic potash (16.5 grams) in 150 cc. of water. This reaction like the two preceding was carried out below 5°. The nearly white precipitate, obtained with cold dilute acetic acid, did not react with potassium iodide; thus showing the absence of bromamide. From hot glacial acetic acid the body crystallizes on cooling in spherical aggregates of almost colorless needles melting at 243°–247°. Very slight decomposition seems to take place on boiling with acetic acid. After several recrystallizations from benzene, in which the body is but slightly soluble, the substance is pure white, and melts at 250°. The new body was proved to be 3-5-dibromcarbonylaminophenol,



by its analysis, by its reduction to carbonylaminophenol, and by its synthesis from 3-5-dibromsalicylic amide.

0.3790 gram gave 17.5 cc. N_2 at 23.5° and 738.6 mm.

	Calculated for $C_7H_3Br_2NO_2$.	Found.
N	4.79	5.07

Jakoby[1] has made a dibromcarbonylaminophenol (m. p. 243°–245°), by the action of bromine water on a water solution of carbonylaminophenol. When a sample of the substance, prepared according to Jakoby, was compared with the above substance the two were found to have quite similar properties, but that they were not identical was shown by the melting-point (about 210°) of a mixture of the two; each substance, separately, melts 35–40° higher. The reduction of both of the above bodies to carbonylaminophenol is readily accomplished.

[1] J. prakt. Chem., [2] **37**, 51.

Reduction of Dibromcarbonylaminophenol.—0.2 gram of Jakoby's dibrom body was shaken thirty minutes with 10 grams of 2½ per cent. sodium amalgam and 25 cc. of water; the body, being readily soluble in alkali, soon dissolved. After filtering from mercury and acidifying, the white precipitate formed was crystallized from hot water. It formed colorless needles, free from bromine, melting at 138°, and having all the properties of carbonylaminophenol; by mixing with pure carbonylaminophenol, the melting-point remained unchanged.

One gram of the dibrom body from salicylic amide was reduced by sodium amalgam as above. The precipitate with acid was free from bromine; from hot water it crystallized in colorless needles, which melt at 138°. The properties of the substance are those of carbonylaminophenol; its complete identity with this body was established by the melting-point, 138°, of their mixture. The last experiment furnishes conclusive proof that the dibrom body obtained by the action of hypobromite on salicylic amide is a dibrom derivative of carbonylaminophenol.

The isomerism of the body obtained from salicylic amide, with that obtained by brominating carbonylaminophenol directly, pointed to a bromination of the aromatic ring as the first step of the reaction of hypobromite on salicylic amide.

Synthesis of 3-5-Dibromcarbonylaminophenol. — Salicylic amide reacts with aqueous bromine with the greatest ease, forming 3-5-dibromsalicylic amide.[1] To a solution of 10 grams of 3-5-dibromsalicylic amide, made according to Spilker, and 4 grams (2 molecules) of caustic potash in 180 cc. of water, cooled to 0°, was added slowly an ice-cold solution of hypobromite resulting from 5.4 grams (1 molecule) of bromine and 5 grams (2½ molecules) of caustic potash in 60 cc. of water. A white crystalline mass resulted. The crystals, which were evidently the potassium salt[2] of the dibromcarbonylaminophenol, were filtered from a slightly colored mother-liquor; dissolved in 250 cc. of water, and an excess of dilute acetic acid added. The white amorphous precipitate formed was filtered off; washed with water, in which it is

[1] Spilker: Ber. d. chem. Ges., **22**, 2769. [2] *Vide*, p. 119.

nearly insoluble; and dried on a clay plate. The yield was 6.7 grams. After recrystallization from hot benzene the substance was perfectly pure. It had the melting-point, 250°, and all the properties of the body obtained by the action of 3 molecules of hypobromite on salicylic amide; by mixing with the latter, the melting-point remained unchanged. A bromine determination confirmed the identity.

0.1303 gram heated with lime gave 0.1674 gram AgBr.

	Calculated for $C_7H_3Br_2NO_2$.	Found.
Br	54.61	54.80

The first product of the action of hypobromite on salicylic amide is, therefore, 3-5-dibromsalicylic amide:

$$C_6H_4.OH.CONH_2 + 2NaOBr \rightarrow C_6H_2Br_2.OH.CONH_2 + 2NaOH.$$

This, by the action of another molecule of hypobromite, must give 3-5-dibromsalicylic bromamide:

$$C_6H_2Br_2.OH.CONH_2 + NaOBr \rightarrow C_6H_2Br_2.OH.CONHBr + NaOH.$$

The bromamide undergoes rearrangement so rapidly that it at once gives the isocyanate[1]:

$$(C_6H_2Br_2.OH)CONHBr + NaOH \rightarrow (C_6H_2Br_2.OH).CO-N< \rightarrow (C_6H_2Br_2.OH.)N=CO.$$

The latter reacts immediately with the neighboring phenol-hydroxyl group to give the product obtained:

$$(C_6H_2Br_2.OH.)N=CO \rightarrow O-C_6H_2.Br_2NH-CO.$$

The great ease with which dibromsalicylic bromamide is rearranged is remarkable. In no other case has such a rearrangement taken place so rapidly, that the bromamide could not be isolated.

Aside from the ease with which the process takes place, the whole series of reactions is perfectly normal.

Salts of Dibromcarbonylaminophenols.—Both dibromcarbonylaminophenols form salts with alkalies. The potassium salt of Jakoby's body was obtained as well-formed white

[1] Stieglitz: This JOURNAL, 18, 75.

needles, by the addition of an excess of 30 per cent. caustic potash to a clear solution of the dibrom body dissolved in a little dilute solution of caustic potash. The salt was purified by dissolving it in acetone, in which it is readily soluble, and adding ligroin (boiling-point 60°–70°), when the salt separated in beautiful white needles, which decompose above 300°. The analysis was made by dissolving the salt in water, adding $\frac{N}{10}$-hydrochloric acid in slight excess, and titrating back with $\frac{N}{10}$-potassium hydroxide using methyl orange. The dibrom body was precipitated by the acid, but was not filtered off, as it does not affect the indicator.

0.4739 gram required 14.6 cc. $\frac{N}{10}$-HCl; calculated for $C_7H_2Br_2NO_2K$, 14.3 cc.

The sodium salt, white needles, was prepared similarly.

0.7525 gram required 24.2 cc. $\frac{N}{10}$-HCl; calculated for $C_7H_2Br_2NO_2Na$, 23.9 cc.

The salts of 3-5-dibromcarbonylaminophenol resemble the above salts, but are more soluble in water and acetone.

The Action of Phosphorus Pentachloride on Dibromcarbonylaminophenol.—Attempts[1] to obtain chormethenylaminophenol by the action of phosphorus pentachloride on carbonylaminophenol have led to a mixture of bodies chlorinated in the ring. The action of phosphorus pentachloride on Jakoby's dibromcarbonylaminophenol was tried with the hope that, owing to the protection afforded by the halogen already in the ring, a chlormethenyldibromaminophenol would result, by a smooth reaction. It was found that phosphorus pentachloride does not act on the dibrom body when the two are heated with dry, boiling chloroform, in which the dibrom body is somewhat soluble; neither do the dry substances react when heated all day in a sealed tube at 100°. At 200° a reaction took place; the tube contained hydrochloric acid, and the black residue had the odor of phosphorus oxychloride. About one-third of the material used was recovered unchanged, but no other pure substance could be isolated.

[1] Bender: Ber. d. chem. Ges., **19**, 2271; Chelmiki: *Ibid.*, **20**, 178.

The Action of Phosphorus Pentachloride on the Sodium Salt of Carbonylaminophenol.

Carbonylaminophenol was prepared according to Bender's[1] method, from his so-called ethyl aminophenylcarbonate, $H_2N—C_6H_4—OCOOC_2H_5$. The latter was made from ethyl *o*-nitrophenylcarbonate. Instead of using an alcoholic solution of potassium nitrophenol, I treated the aqueous solution of the potassium salt with chlorcarbonic ether and obtained quantitative yields of ethyl nitrophenylcarbonate, which I found distils with no apparent decomposition at 176°–178° under 21 mm. pressure. It was found too that alcohol could be omitted with advantage, in the reduction which is readily accomplished when concentrated hydrochloric acid is added in small portions to a mixture of tin and the ester, the flask being cooled to prevent much rise of temperature. After diluting the solution of the reduced substance with an equal volume of water, and filtering from the remaining tin and sediment, a perfectly clear and colorless solution is obtained. This solution may be kept several hours without showing signs of crystallization, but slowly deposits pure white crystals on prolonged standing. If, however, the clear solution is heated to 90° for 10 minutes, it becomes very turbid with oily drops, and on cooling the whole of the reduction product separates *at once* in the form of white crystals. The latter are now insoluble in dilute acids, but dissolve readily in alkalies. In spite of the fact that the body is an *acid* and *not a base*, Bender described it as aminophenylethyl carbonate, $NH_2—C_6H_4—OCOOC_2H_5$, which no doubt exists at first in the acid solution obtained in the reduction. Mr. J. H. Ransom[2] working in this laboratory, on this subject with Dr. Stieglitz has now proved that a rearrangement takes place in the acid solution leading to the formation of oxyphenylurethane, $C_2H_5O_2CNHC_6H_4OH$ or $NH—C_6H_4—O—C(OH)OC_2H_5$.

The results of this investigation will be published at a later date in this Journal.

[1] Ber. d. chem. Ges., 19, 2269. [2] *Ibid.*, 31, 1055.

By heating the above urethane to 230° it was converted into carbonylaminophenol, with loss of alcohol.

Upon mixing a concentrated solution of carbonylaminophenol in absolute alcohol with the calculated amount of alcoholic sodium ethylate, a gray crystalline precipitate of the sodium salt is formed, the amount of which is increased by the addition of ligroin. The salt is very easily soluble in water and in alcohol; with dilute acids, even carbonic acid, carbonylaminophenol is regenerated.

The dry sodium salt was treated with phosphorus pentachloride, under various conditions, with the hope of obtaining chlormethenylaminophenol. The reaction was always complicated, giving a mixture of products from which very little and often none of the desired body could be isolated. It was thought possible that ethoxymethenylaminophenol, $O—C_6H_4—N=C—OC_2H_5$, might be converted into chlormethenylaminophenol by the action of phosphorus pentachloride. This ester has been made from *o*-aminophenol and imido-carbonic ester[1]; but for this experiment it was prepared by the action of alcohol and sodic hydrate on chlormethenylaminophenol, which latter is readily obtained in another way (see below). The body thus made had the boiling-point and other properties ascribed to it by Sandmeyer. By heating with aqueous hydrochloric acid it was readily split into carbonylaminophenol and ethyl chloride. The ester reacts with phosphorus pentachloride only on heating, but no chlormethenylaminophenol was found in the resulting product.

The experiments just described prove that it is impossible to replace the carbonyl oxygen in carbonylaminophenol by halogen by any possible variation of the conditions. They show that it is extremely unlikely, that the action of phosphorus pentachloride on any urethane takes place according to the equation:

$$RNHCOOR + PCl_5 = RNHCCl_2OR + POCl_3.$$

As these methods failed to lead to chlor- and brommethenylaminophenols, I returned to Seidel's method for the preparation of the former body; *viz.*, by the action of phosphorus

[1] Sandmeyer: Ber. d. chem. Ges., 19, 2655.

pentachloride on thiocarbamidophenol. In this reaction, besides the body desired, other products containing chlorine and phosphorus were also obtained, as has already been observed by Seidel. The separation of pure chlormethenylaminophenol from these by-products and the phosphorus sulphochloride formed is very troublesome, and the yield is usually poor; while with phosphorus pentabromide not a trace of the corresponding brommethenylaminophenol was obtained.

The chlorinating effect of phosphorus pentachloride made it seem probable, that, in Seidel's reaction, the formation of chlormethenylaminophenol was chiefly due to the action on the thio body of chlorine, liberated from phosphorus pentachloride at the temperature used. If this were true, by using chlorine alone, under the most favorable conditions, a much smoother reaction should occur.

As a precedent, the case of phenyl mustard-oil may be mentioned; when heated with phosphorus pentachloride[1] this gives a mixture of phenylimidocarbonyl chloride, chlormethenylaminothiophenol and other chlorinated products; while, by the action of chlorine[2] *in the cold*, Nef[3] has obtained only phenylimidocarbonyl chloride, in almost quantitative yield:

$$C_6H_5NCS + 2Cl_2 \rightarrow C_6H_5NCCl_2 + SCl_2.$$

The following reaction shows the correctness of the above assumption.

The Action of Chlorine on o-Thiocarbaminophenol:—Chormethenylaminophenol, $O{-}C_6H_4{-}N{=}CCl$.

Ten grams of finely powdered and carefully dried *o*-thiocarbaminophenol, made according to Dünner,[4] was suspended in 100 grams of perfectly dry chloroform free from alcohol, in which the thio-body is not very soluble; and carefully dried chlorine slowly passed into the mixture. The flask was cooled with water to prevent a rise of temperature above 20°. The chlorine is readily absorbed at first, and the stream is continued until absorption no longer takes place. The chloroform solution, in which the reaction-products are easily solu-

[1] Hofmann: Ber. d. chem. Ges., **12**, 1127. [2] Sell and Zierold: *Ibid.*, **7**, 1228.
[3] Ann. Chem. (Liebig), **270**, 284. [4] Ber. d chem. Ges., **9**, 465.

ble, is poured slowly, with vigorous shaking, into half a liter of cold water, in order to decompose the sulphur dichloride formed. After washing with dilute caustic soda and water, until no odor of chlorine or sulphur chloride remained, the chloroform solution was dried with calcium chloride and distilled. 9.2 grams of nearly colorless oil resulted, which, on redistillation gave 8.5 grams of a pure colorless oil, boiling at 200°. The substance has the boiling-point, the odor, and other properties of chlormethenylaminophenol, obtained by the action of phosphorus pentachloride on thiocarbaminophenol. With aqueous hydrochloric acid it is readily decomposed, giving carbonylaminophenol (m. p. 138°). Its index of refraction, as determined with the Abbey refractometer, at 20°, is 1.5678.

Brommethenylaminophenol, $O\text{—}C_6H_4\text{—}N{=}CBr$.

As has already been stated, the action of phosphorus pentabromide on thiocarbaminophenol does not give the above bromide; neither is the chlorine in chlormethenylaminophenol replaced by bromine by treating the chlor body with an excess of bromine. Attempts to prepare the bromide by a method similar to that by which the chloride was obtained (*viz.*, by the direct action of halogen on thiocarbaminophenol) were not at first successful.

According to the equation,

$$O.C_6H_4.NH.CS + 2Br_2 = O.C_6H_4.N : CBr + HBr + SBr_2,$$

two molecules of bromine are required for each molecule of the thio-body; and this was the amount used in the first experiments which proved unsuccessful. Only when much more bromine (7 to 8 atoms) is used can the bromide be obtained. 38 grams of bromine, in 50 grams of pure *dry* chloroform, were added very slowly, with constant shaking, to 10 grams of thiocarbaminophenol, suspended in 75 grams of pure dry chloroform. At first a heavy brick-red precipitate is formed; but, with an excess of bromine this changes to a heavy, insoluble, dark oil. After adding the bromine, which requires perhaps three-quarters of an hour, the mixture is

allowed to stand a short time; then treated with water and sodic hydrate, as in the preparation of chlormethenylaminophenol. The treatment with water causes the insoluble oil to become soluble in chloroform; the latter, after drying with calcium chloride, was distilled off, leaving an oily residue. This oily residue, consisting chiefly of brommethenylaminophenol, was treated with ligroin (b. p. 40–60°), which dissolves the brom-body leaving a small, dark residue. Its purification is best accomplished by passing into the ligroin solution pure dry hydrogen bromide, which precipitates the hydrobromide of brommethenylaminophenol. This is filtered off and treated with much water, which causes an immediate decomposition into hydrobromic acid and brommethenylaminophenol; the latter is again taken up in ligroin, and the dried ligroin solution again precipitated with hydrogen bromide. After repeating the precipitation and treatment with water several times, the dried ligroin solution was evaporated in a vacuum, and the last traces of ligroin removed in a current of dry air, in the presence of potassium hydroxide and paraffin. On cooling with ice-water, white crystals were obtained, melting at 27°. These were brommethenylaminophenol as the following analysis shows:

0.2838 gram required 14.2 cc. $\frac{N}{10}$ $AgNO_3$.

	Calculated for C_7H_4BrNO.	Found.
Br	40.40	40.03

The analysis was made by treating the substance with alcohol and dilute sodic hydrate, when the following reaction[1] takes place:

$$O{-}C_6H_4{-}N{=}CBr + HOR + NaOH \rightarrow O{-}C_6H_4{-}N{=}COR + NaBr + H_2O.$$

The solution was acidulated with nitric acid and titrated according to Volhard.

Chlormethenylaminophenol Hydrochloride:—Dichlorcarbonylaminophenol, $O{-}C_6H_4{-}NH{-}CCl_2$.

Carefully dried hydrogen chloride is passed into 0.5 gram of

[1] *Vide*, p. 122.

chlormethenylaminophenol dissolved in 8 cc. of dry low-boiling ligroin, in a well-stoppered vessel, provided with an exit tube. Beautiful white crystals are soon deposited on the walls of the vessel. When the quantity of crystals no longer increases, the liquid is poured off completely and 4–5 cc. of fresh ligroin added, and again decanted. The latter operation is accomplished as quickly as possible to avoid absorption of moisture from the air. The crystals are then freed from ligroin in a current of dry hydrogen chloride, a pump being used to secure a partial vacuum. In a short time the ligroin has evaporated, but a portion of the hydrochloride has decomposed into its constituents. More hydrogen chloride is then passed in until the crystals appear free from oil. The new substance is the very unstable hydrochloride of chlormethenylaminophenol. It is stable only in an atmosphere of dry hydrogen chloride at very nearly atmospheric pressure. It decomposes into its constituents very rapidly in a vacuum, or in dry air, where the partial pressure of hydrogen chloride is also zero. As might be expected it is instantly decomposed by water. A small amount of the hydrochloride, made in a small test-tube, was heated in a water-bath, while a current of dry hydrogen chloride was passed through the tube. Under these conditions the substance melts with decomposition at 57°–58° (thermometer in bath).

The analysis of such an unstable compound cannot, of course, be made by ordinary methods, but was accomplished by quickly bringing the freshly prepared crystals upon a watch-glass, moving this through the air *3 or 4 seconds* to free them from adhering hydrogen chloride, and *immediately* pouring the substance into a tared, wide-mouthed weighing-bottle, containing 25 to 30 cc. of water, and weighing again. The crystals are decomposed at once into hydrochloric acid and chlormethenylaminophenol, which settles to the bottom as a colorless oil. Methyl orange was added and the solution titrated with $\frac{N}{10}$-alkali. In neutral or alkaline solution chlormethenylaminophenol is attacked only very slowly by water. In concentrated acid solution, however, it is soluble, and the decomposition by water goes on quite rapidly; but, at the di-

lution used in the analysis, the decomposition is inappreciable.

Substance. Gram.	Calculated for $C_7H_5NOCl_2$ (one mol. of acid) cc. tenth-normal alkali.	Found. cc.
0.1720	9.05	8.65
0.1024	5.39	5.24

Considering the great instability of the body, these figures are as good as could be expected.

Chlormethenylaminophenol Hydrobromide :—Chlorbromcarbonyl-aminophenol, $O—C_6H_4—NH—CClBr$.

One gram of chlormethenylaminophenol was dissolved in 40 cc. of low-boiling ligroin and treated with dry hydrogen bromide. The hydrobromide of chlormethenylaminophenol appears immediately as a white precipitate, which is much more stable than the hydrochloride. The precipitate was quickly filtered off with a pump, pressed on a clay plate a few moments, and dried in a vacuum over potassium hydroxide for about five minutes. The analysis was made as in the case of the dichloride.

	Substance. Gram.	Calculated for $C_7H_5NOClBr$ (one mol. of acid) cc. tenth-normal alkali.	Found. cc.
I.	0.3420	14.58	14.35
II.	0.1590	6.78	6.86

The substance is a white powder, which melts at 155° with decomposition. It quickly loses one molecule of acid in contact with water.

The neutralized solution, in analysis II. above, was separated from the insoluble oil and precipitated with silver nitrate. A weighed portion of the dried silver haloid was reduced to metallic silver.

I. 0.1193 gram of the dry silver salt gave 0.0693 gram Ag.

A second preparation of silver haloid was made from the solution resulting from the action of water on another sample of freshly prepared hydrobromide.

II. 0.2220 gram of the dry silver salt gave 0.1304 gram Ag.

	Calculated for AgCl.	Calculated for AgBr.	Found. I.	II.
Halogen	24.73	42.55	41.91	41.26

The result shows that, by the action of water on chlormethenylaminophenol hydrobromide, hydrobromic acid is split off almost without any hydrochloric acid.

Brommethenylaminophenol Hydrobromide:—Dibromcarbonylaminophenol, $O—C_6H_4—NH—CBr_2$.

By passing dry hydrogen bromide into a ligroin solution of brommethenylaminophenol, the hydrobromide is obtained as an almost colorless precipitate. It was dried and analyzed exactly as was the hydrobromide of chlormethenylaminophenol. The new salt melts with decomposition at 163°, and is decomposed by contact with water.

Substance. Gram.	Calculated for $C_7H_5NOBr_2$ (one mol. of acid) cc. tenth-normal alkali.	Found. cc.
0.1451	5.20	5.31

Brommethenylaminophenol Hydrochloride:—Chlorbromcarbonylaminophenol, $O—C_6H_4—NH—CBrCl$.

A ligroin solution of brommethenylaminophenol was precipitated by dry hydrogen chloride. The nearly white precipitate resembles the hydrobromide of chlormethenylaminophenol in every respect, except in having a slight tinge of color, due to the fact that perfectly pure and colorless brommethenylaminophenol was not used, on account of the difficulty of preparing it. The new salt melts, with decomposition, at 155°, which is also the melting-point of the hydrobromide of the chlor-body. The melting-point of a mixture of the two freshly prepared salts is also 155°. The new body is decomposed at once by water, *hydrobromic acid being chiefly split off*, with only traces of hydrochloric acid.

	Substance. Gram.	Calculated for $C_7H_5NOBrCl$ (one mol. of acid) cc. tenth-normal alkali.	Found. cc.
I.	0.3414	14.56	12.83
II.	0.2580	11.00	10.68
III.	0.2279	9.72	9.42

The filtrate from analysis I. was precipitated by silver nitrate and a portion of the silver halide reduced to silver.

I. 0.2195 gram of the dry silver salt gave 0.1301 gram Ag. Another filtrate from some freshly prepared hydrochloride of the brom-body treated with water, was precipitated with silver nitrate.

II. 0.3967 gram of the dry silver salt gave 0.2299 gram Ag.

	Calculated for AgCl.	Calculated for AgBr.	Found. I.	Found. II.
Halogen	24.73	42.55	40.73	42.05

As evidence of the identity of the hydrobromide of chlormethenylaminophenol and the hydrochloride of brommethenylaminophenol we have the agreement in physical properties and melting-point and the fact that their mixture melts at the same temperature; but, since the bodies melt with some decomposition, it does not necessarily follow that their identity is absolutely proved by this latter fact as would be the case with bodies that melt without decomposition. However, the behavior with water, by which both split off chiefly hydrobromic acid with only traces of hydrochloric acid, is a fact which is inexplicable on any ground except the identity of the two bodies. The identity of these bodies justifies, therefore, the constitutions already ascribed to them; all of the halogen is consequently attached to carbon. That, moreover, these bodies are true salts was shown by the preparation of other salts and by obtaining ionic reactions in aqueous solutions.

Chlormethenylaminophenol Nitrate, $O.C_6H_4—NH.C.Cl.ONO_2$.

Seidel states[1] that with concentrated nitric and hydrochloric acids chlormethenylaminophenol gives beautiful crystalline salts; but he does not give analyses nor further data, proving that these are really salts of chlormethenylaminophenol. The nitrate is readily obtained by treating the oil (0.3 to 0.4 gram) with 10 cc. of nitric acid (sp. gr. 1.28) at 0°. The oil dissolves and white crystals separate at once. These were quickly drained on a platinum cone with the aid of a pump,

[1] J. prakt. Chem. [2], **42**, 455.

rubbed on a clay plate for a minute or two, and then dried over sulphuric acid in a vacuum, for 30 to 40 minutes. If the nitric acid is too concentrated or is allowed to remain in contact with the crystals too long, or if the temperature is allowed to rise much above 0° the salt becomes yellow, apparently on account of nitrification. The nitrate forms beautiful white crystals, which become yellow and finally brown on being kept a few hours in a desiccator. In contact with water the salt suffers complete hydrolysis into chlormethenylaminophenol and nitric acid. The analysis was made by bringing the dried crystals into a large, tared, wide-mouthed weighing-bottle, weighing quickly, then adding water and a drop of methyl orange and titrating with $\frac{N}{10}$-alkali.

	Substance. Gram.	Calculated for $C_9H_4ClNO.HNO_3$. cc. tenth-normal alkali.	Found. cc.
I.	0.2592	12.0	11.8
II.	0.3974	18.4	19.0

The substance used in analysis II. had become slightly yellow; that in I. was pure white. A test of the solutions, after titrating in the above analysis, showed only traces of chlorine.

The Action of Hydrochloric Acid on Chlormethenylaminophenol.

When chlormethenylaminophenol is treated with cold concentrated hydrochloric acid it dissolves very readily and the oil separates out unchanged if water is added immediately. The solution in concentrated hydrochloric acid gives no crystals at once, but after standing an hour at 0° white crystals are deposited in considerable quantity. These have all the properties of carbonylaminophenol; they are not soluble in water nor are they decomposed by water, but dissolve readily in alkalies with acids. The alkaline solution gives white crystals, containing no chlorine, which are undoubtedly carbonylaminophenol. Even by the use of a solution of hydrochloric acid saturated at 0°, it was not possible to obtain the hydrochloride in the solid form. It is therefore probable that Seidel mistook the crystals of carbonylaminophenol, for those of the hydrochloride of chlormethenylaminophenol. That the salt exists in solution, being very soluble, was shown by the action of nitric acid on a freshly prepared

solution of the hydrochloride, and by the formation of a chlorplatinate.

A few drops of chlormethenylaminophenol were dissolved in about two volumes of concentrated hydrochloric acid. No crystals were formed, even on cooling the solution with ice and salt; the addition of nitric acid (sp. gr. 1.28) caused an immediate heavy white precipitate, which was undoubtedly the nitrate, since on the addition of water the crystals decomposed, leaving an oil—chlormethenylaminophenol. The formation of the nitrate in this way must be considered a true ionic reaction, and shows clearly that the bodies under discussion are true salts.

Chlormethenylaminophenol Chlorplatinate,

$$(O.C_6H_4.NH.C.Cl)_2PtCl_6.$$

0.5 gram of chlormethenylaminophenol was dissolved in about 4 cc. of ice-cold concentrated hydrochloric acid and added to a solution of 0.5 gram of platinic chloride dissolved in 3 cc. of concentrated hydrochloric acid. After ten minutes the ice-cold solution had deposited a considerable quantity of orange-colored crystals. These were drained on a platinum cone, pressed out quickly on a clay plate, and dried over sulphuric acid. The crystals are stable in the absence of water, but the latter quickly decomposes the body into its constituents.

0.0529 gram gave 0.0141 gram Pt.

0.2334 gram gave 0.0619 gram Pt.

	Calculated for $(C_7H_4ClNO)_2PtCl_6$.	Found. I.	II.
Pt	26.79	26.69	26.52

PART II.

The Hydrochlorides of Carbodiphenylimide.[1]

Carbodiphenylimide unites with hydrochloric acid, as Lengfeld and Stieglitz have found,[2] in two proportions; namely, to form the monohydrochloride, $C(C_6H_5N)_2.HCl$, and the dihydrochloride, $C(C_6H_5N)_2.2HCl$. From the fact that the monohydrochloride gives with sodium ethylate, smoothly

[1] Preliminary reports: Ber. d. chem. Ges., **30**, 1090, 1682.

[2] This JOURNAL, **17**, 107.

and quantitatively, ethyl isocarbanilide, $C_2H_5OC(NHC_6H_5):NC_6H_5$, Lengfeld and Stieglitz[1] have thought it quite probable that, in the monochloride, the chlorine is bound to carbon and not to nitrogen; that it has consequently the constitution, $Cl.C(NHC_6H_5):NC_6H_5$. Similarly, in the dihydrochloride, one, at least, and perhaps both chlorine atoms are bound to carbon thus: $ClC(NHC_6H_5):NC_6H_5.HCl$ or $Cl_2C(NHC_6H_5)_2$. In the hope of obtaining further evidence on this point, I have studied the action of the above hydrochlorides on benzene, in the presence of aluminium chloride. According to the view just expressed, it seemed possible, in this way, to obtain benzamidine (or benzophenone) derivatives,[2] according to:

$$C_6H_6+ClC(NHC_6H_5):NC_6H_5 \longrightarrow C_6H_5\overset{*}{C}(NHC_6H_5):NC_6H_5.HCl;$$

$$\text{and } 2C_6H_6+Cl_2\overset{*}{C}(NHC_6H_5):NC_6H_5 \rightarrow (C_6H_5)_2\overset{*}{C}(NHC_6H_5)_2+$$

$$2HCl \rightarrow (C_6H_5)_2\overset{*}{C}=NC_6H_5+C_6H_5NH_2.HCl+HCl.$$

[1] *Loc. cit.*; and Stieglitz: Ber. d. chem. Ges., **28**, 537.

[2] Since Friedel and Crafts' syntheses with aluminium chloride involve, almost universally, the use of an alkyl or acyl haloid—that is, substances containing the group CCl, or its equivalent, it is thought that the reaction can be used to prove the presence of such a CCl group, in a chloride of doubtful constitution. This method of proof had, in fact, been previously used, most notably by Gattermann (Ann. Chem. (Liebig), **244**, 47), in the closely allied case of the hydrochlorides of the isocyanates. According to their action on benzene derivatives, in the presence of aluminium chloride, they have been generally assumed to be chlorformanilides (*Vide*, Meyer and Jacobson: Lehrbuch, Vol. II., p. 199; Richter-Anschütz, 8th ed., Vol. II., p. 76)

$$RN.CO + HCl \longrightarrow RNH.COCl.$$

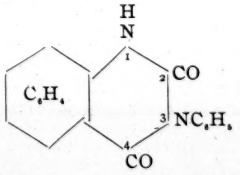
In fact, in their action on benzene, in the presence of aluminium chloride, they resemble substances which undoubtedly have a similar constitution, such as chlorformmethylanilide, $RNCH_3.COCl$. In the few cases where Friedel and Crafts' synthesis has succeeded without the use of an alkyl or acyl haloid—for instance, with phenyl isocyanate (Leuckart: Ber. d. chem. Ges., **18**, 873) and with ethylene (Balson: Bull. Soc. chim., **31**, 541), it appeared most probable that such haloids were first formed by the addition of hydrogen chloride, which is always present (Leuckart; *Loc. cit.*; Gattermann: *Loc. cit.*).

The two most important interpretations of Friedel and Crafts' reaction agree with this conclusion: the older one (Friedel and Crafts: Ann. Chim. [6], **14**, 457; Meyer u. Jacobson: Lehrbuch, II, 98) requiring a chlor-carbon group (CCl) to react with the supposed intermediate organic derivative of aluminium chloride, *e. g.*, $C_6H_5.Al_2Cl_5$; the new and interesting view of Nef (Ann. Chem. (Liebig), **298**, 222) ascribing the condensation to the addition of phenyl and hydrogen (C_6H_5 and H) to the nascent double bonds of unsaturated derivatives, and thus postulating the presence of the same chlor-carbon group, to make a "nascent double bond" at all possible.

However no benzamidine nor benzophenone derivatives are formed. The chief product of the reaction is a yellow base, of the composition $C_{26}H_{20}N_4$, the constitution of which has been established by a thorough study of its reactions, its decomposition-products, and finally by its direct synthesis. The results leave no doubt that a Friedel and Crafts' condensation actually takes place involving the carbon atom marked with a star ($\overset{*}{C}$); only instead of attacking the benzene itself, it enters one of the benzene nuclei of a second molecule of carbodiphenylimide. The composition of the new body is the same as that of carbodiphenylimide itself, but preliminary determination showed the body to have double the molecular weight of carbodiphenylimide. It has therefore the composition $C_{26}H_{20}N_4$. Several polymers of carbodiphenylimide are described in the literature;[1] but the body obtained by the action of aluminium chloride differs markedly from all of these and from carbodiphenylimide itself. The body $C_{26}H_{20}N_4$ is a base, forming yellow crystals, which dissolve readily in dilute hydrochloric acid, to form a yellow solution, that soon becomes colorless. Alkalies precipitate from the colorless solution a white base, having the composition $C_{20}H_{18}N_2O$, while the aqueous solution contains aniline. Saponification of an aniline group has therefore taken place:

$$C_{26}H_{20}N_4 + H_2O \longrightarrow C_{20}H_{18}N_2O + C_6H_5NH_2.$$

By further saponification of the substance $C_{20}H_{18}N_2O$ by prolonged heating, in a sealed tube, with concentrated hydrochloric acid, a good yield of a body $C_{14}H_{10}N_2O_2$, which proved to be identical with the 3-phenyl-2-4-diketotetrahydroquinazoline of Busch[2] and Paal,[3]



[1] Weith: Ber. d. chem. Ges., **7**, 10; Schall: *Ibid.*, **25**, 2886; Cf. Von Miller u. Plöchl: *Ibid.*, **28**, 1004.

[2] J. prakt. Chem., **51**, 265.

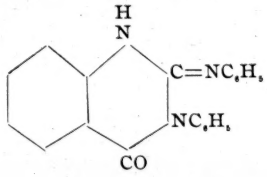
[3] Ber. d. chem. Ges., **27**, 978.

was obtained, and at the same time aniline was formed. The action of concentrated hydrochloric acid on the white base, $C_{20}H_{18}N_2O$, is therefore expressed by the equation :

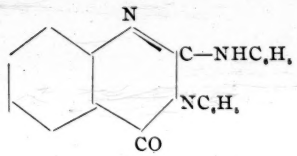
$$C_{20}H_{18}N_2O + H_2O \longrightarrow C_{14}H_{10}N_2O_2 + C_6H_5NH_2.$$

The compound $C_{20}H_{18}N_2O$ must consequently have the constitution expressed by one of the following structural formulas:

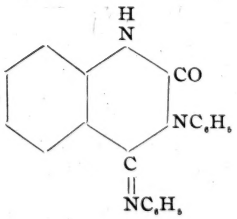
Ia.

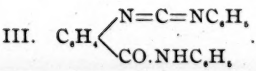


Ib.



II.



III. 

Formula III is excluded by the following properties of the body : (1) it is a strong base soluble in dilute acids ; (2) it remains unchanged when boiled with concentrated hydrochlo-

ric acid, as also when boiled with aniline. I*a* and I*b* differ from II only in the position of the aniline group attached to the quinazoline ring. Since the aniline group in position 2 (I*a* or *b*) forms a derivative of triphenylguanidine, which is very stable toward saponifying agents, while in position 4 (II), we have a derivative of *s*-benzenyldiphenylamidine, which is readily saponified to benzanilide,[1] formula I (*a* or *b*) was supposed to be the more probable one, and this view was tested by preparing a body of the composition and constitution I. It proved to be identical with the white base, $C_{20}H_{15}N_3O$. The compound is, therefore, either 2-phenylimido-3-phenyl-4-ketotetrahydroquinazoline, I*a*; or 2-phenylamido-3-phenyl-4-ketodihydroquinazoline, I*b*.

Two substances corresponding to I*a* and I*b* are so closely related and pass over so readily into one and the same form that only one form is usually, if not always, known. Experiments will be described below, the object of which is to distinguish between these two forms.

With methyl iodide, the body gives the 1(N) methyl derivative, indicating, perhaps, formula I*a*, on which account, to avoid the duplication of cumbersome names, that of formula I*a* will be used in referring to the body and its derivatives. As, however, addition of the methyl iodide to the double bond between carbon and nitrogen, and subsequent splitting off of hydrogen iodide, may take place instead of direct substitution, this reaction is not free from objection, as a means of determining constitution, so that formula I*b* is not absolutely excluded.

The synthetic proof of the constitution of the white base, $C_{20}H_{15}N_3O$, was furnished in the following manner: From anthranilic acid and phenyl mustard-oil, *o*-phenylthioureïdobenzoic acid was prepared. The latter, by loss of water, readily gives 2-thio-3(N)-phenyl-4-ketotetrahydroquinazoline:

$$C_6H_4.NH_2.COOH + C_6H_5NCS \rightarrow C_6H_5\text{–}N\text{–}CO\text{–}C_6H_4\text{–}NH\text{–}C{=}S + H_2O.$$

This compound, as also its thio-ether, 2-ethylthio-3(N)-phenyl-4-ketodihydroquinazoline, proved to be unusually in-

[1] Wallach: Ann. Chem. (Liebig), **184**, 85.

active towards aniline; both, however, when heated with aniline in a sealed tube to 300°, gave a small amount (5 to 10 per cent. yield) of the compound $C_{20}H_{15}N_3O$, with evolution of hydrogen sulphide or ethylmercaptan. Since the thio-bodies reacted with aniline with such great difficulty, another method of synthesis was tried, and this gave, without difficulty, the desired compound. If one treats the 2-thio-3(N)-phenyl-4-ketotetrahydraquinazoline with dry chlorine, in the presence of chloroform, the sulphur is easily replaced by chlorine, with the formation of 2-chlor-3(N)-phenyl-4-keto-dihydroquinazoline, thus:

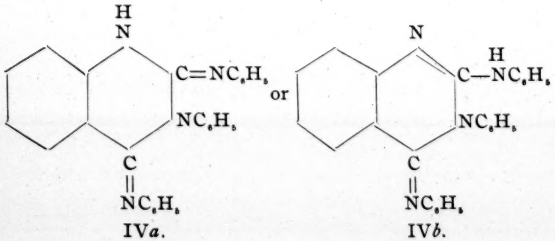
$$C_6H_5N\text{—}CO\text{—}C_6H_4\text{—}NH\text{—}CS + 2Cl_2 \longrightarrow$$

$$C_6H_5N\text{—}CO\text{—}C_6H_4\text{—}N{=}CCl + SCl_2 + HCl.$$

The chloride so obtained gave, smoothly and quantitatively, by heating with aniline, the compound $C_{20}H_{15}N_3O$. This body has, therefore, the aniline group in position 2, [formula I (*a* or *b*)].

This synthesis shows at the same time that the quinazoline double ring is not formed in the heating of this compound with concentrated hydrochloric acid in the sealed tube; but that it exists previously in the bases obtained from carbodiphenylimide.

The yellow base, $C_{26}H_{20}N_4$, obtained by the action of aluminium chloride on carbodiphenylimide, gives, by saponification with cold dilute hydrochloric acid, aniline and the quinazoline derivative, $C_{20}H_{15}N_3O$, just discussed, and must therefore be represented by one of the closely allied formulas



IV*a*. IV*b*.

It is therefore 2-4-diphenylimido-3(N)-phenyltetrahydroquinazoline (IV *a*) or 2-phenylamido-3(N)-phenyl-4-phenylimidodihydroquinazoline (IV *b*). The yellow compound, $C_{26}H_{20}N_4$, for which the above closely related formulas have been determined, exists in two forms—prisms (α-form) melting at 171°, and rhombic plates (β-form) melting at 184°. With a single possible exception, described below, the two forms have the same chemical properties, but their solubilities, in various organic solvents, are quite different; and when either form is dissolved in any solvent it is always the form which is less soluble in that solvent that crystallizes out. When heated above its melting-point the α-form is converted into the β-form. Whether the two forms are constitutionally different according to IV *a* and *b*, or stereoisomeric phenylimido derivatives, or finally only dimorphic modifications of a single substance, has not yet been definitely determined. This will be discussed in connection with the experiments on this point.

The constitution developed for the yellow base, $C_{26}H_{20}N_4$, was confirmed synthetically in the following way: The above-mentioned 2-chlor-3(N)-phenyl-4-ketodihydroquinazoline was treated with phosphorus pentachloride in order to replace the oxygen atom by chlorine. By treating the compound so obtained with aniline, a small amount of the yellow base, $C_{26}H_{20}N_4$, was obtained as prisms (α-form), melting at 171°, which after melting and cooling crystallized in the β-form, melting at 184°. The body had all the properties of the compound obtained from carbodiphenylimide. The reactions take place thus:

$$C_6H_4\underset{\llcorner\!\!\lrcorner}{\overset{}{\underset{|}{}}}N{-}CO.C_6H_4{-}N{=}CCl + PCl_5 \rightarrow$$

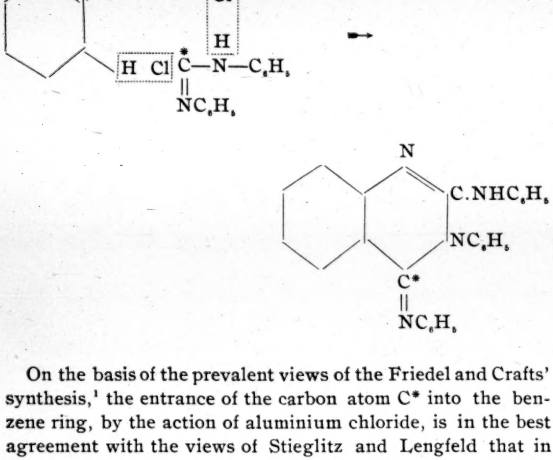
$$C_6H_5N.\underset{\llcorner\!\!\lrcorner}{CCl_2}.C_6H_4{-}N{=}CCl + POCl_3;$$

$$C_6H_4\underset{\llcorner\!\!\lrcorner}{\overset{}{\underset{|}{}}}N{-}CCl_2{-}C_6H_4{-}N{=}CCl + 5C_6H_5NH_2 \rightarrow$$

$$C_6H_4\underset{\llcorner\!\!\lrcorner}{\overset{}{\underset{|}{}}}N.C(:NC_6H_5).C_6H_4.NH.C{=}NC_6H_5 + 3C_6H_5NH_2.HCl.$$

The formation of 2-4-phenylimido-3(N)-phenyltetrahydroquinazoline by the action of aluminium chloride on the hydro-

chloride of carbodiphenylimide may be represented in the following simple manner :



On the basis of the prevalent views of the Friedel and Crafts' synthesis,[1] the entrance of the carbon atom C* into the benzene ring, by the action of aluminium chloride, is in the best agreement with the views of Stieglitz and Lengfeld that in the monohydrochloride of carbodiphenylimide the chlorine is bound to carbon ; that it is therefore to be regarded as chlorformyldiphenylamidine, $ClC(NHC_6H_5):NC_6H_5$.

By using carbodiphenylimide, instead of its hydrochloride, the yield of the yellow base is very materially reduced, being only one-tenth as large as that obtained from the monochloride (5 per cent. instead of 50 per cent. of the theoretical yield) and here, as in Leuckart's results with phenyl isocyanate,[2] benzene and aluminium chloride, the formation of any of the quinazoline compounds at all may be ascribed to the liberation of some hydrogen chloride, which would convert the carbodiphenylimide into the monochloride.

That the chlorine atom in question becomes attached to car-

[1] *Vide* note p. 132. [2] *Loc. cit.*

bon *before* the possible saturation of the free nitrogen valencies, by an excess of hydrogen chloride, as perhaps according to the equation,

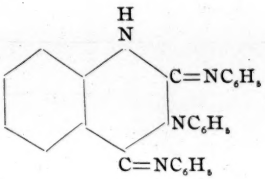
$C(:NC_6H_5.HCl)_2+HCl \rightarrow Cl.C(:NC_6H_5.HCl)(NHC_6H_5.HCl)$,

is proved by the fact that an excess of hydrogen chloride must be avoided in order to accomplish the formation of the quinazoline compound.

EXPERIMENTAL PART.

The Action of Aluminium Chloride on the Chlorides of Carbodiphenylimide.

2-4-Diphenylimido-3(N)-phenyltetrahydroquinazoline,



Carefully dried hydrogen chloride was passed into a solution of freshly prepared carbodiphenylimide (10 grams) in benzene (70 cc.) free from thiophene until a heavy precipitate was obtained. As Lengfeld and Stieglitz[1] have shown, this precipitate consists of a mixture of the two chlorides of carbodiphenylimide, while the benzene solution still contains unchanged imide in solution. The mixture so obtained was diluted with 100 cc. of pure carbon bisulphide; heated to boiling; and 10 grams of aluminium chloride added, in portions of 2 grams in the course of three-quarters of an hour. After heating for a quarter of an hour longer, the nearly colorless benzene and carbon bisulphide solution, which still contained a little unchanged carbodiphenylimide, was poured from the dark-brown mass that had separated during the reaction. The latter was treated with dilute sodic hydrate and with water to remove aluminium compounds; and the yellow resi-

[1] This JOURNAL, 17, 107.

due, excepting a small insoluble portion, was dissolved in carbon bisulphide, in which the product is now very easily soluble. On evaporating the solution at the ordinary temperature, yellow crystals of 2-4-diphenylimido-3(N)-phenyltetrahydroquinazoline separated, the amount of which was increased by adding alcohol.

The body was purified by dissolving in benzene and adding ligroin (b. p. 40–60°). With a small amount of ligroin, a small quantity of sulphur-yellow, rhombic plates (β-form), melting at 184°, was obtained, while the filtrate with more ligroin gave a far greater amount of yellow prisms (α-form), melting at 171°.

0.2097 gram of the α-form gave 0.6150 gram CO_2, and 0.0966 gram H_2O.

0.1062 gram of the α-form gave 0.3141 gram CO_2, and 0.0544 gram H_2O.

0.1976 gram of the α-form gave 24.7 cc. of N_2 at 17.5° and 752.4 mm.

	Calculated for $C_{13}H_{10}N_2$ or $C_{26}H_{20}N_4$.	Found. I.	II.	III.
C	80.41	80.00	80.66	....
H	5.15	5.20	5.68	....
N	14.44	....	....	14.38

As has been mentioned, the yield of the above body depends, to a great extent, upon the amount of hydrogen chloride present during the reaction with aluminium chloride. Under favorable conditions the yield is about 50 per cent. An excess of hydrogen chloride must be avoided. In cases in which very much more than one equivalent of hydrogen chloride was passed into the benzene solution of carbodiphenylimide very little, or with a great excess even none, of the quinazoline resulted. The best yield was obtained by dissolving equivalent quantities of carbodiphenylimide and its pure dry dihydrochloride[1] in benzene, thus securing exactly one equivalent of hydrogen chloride. This procedure is unnecessary if, in the preparation of the chloride, the current of hydrogen chloride is stopped before any of the heavy precipitate first formed begins to dissolve, as at this point

[1] Lengfeld and Stieglitz: This JOURNAL, 17, 107.

approximately one molecule of the gas has been absorbed. It has been found that the best method of separating the body from the by-products, which are chiefly unchanged carbodiphenylimide, polymeric carbodiphenylimide and carbanilide, the latter being formed by the action of water on carbodiphenylimide, consists in treating the mixture, left after removing aluminium compounds, as above described, with cold alcohol in small portions, and dissolving the residue, which is chiefly the new body, in hot acetone and adding 80 per cent. alcohol. On standing, most of the substance separates in prisms of the α-form.

The action of aluminium chloride either on free carbodiphenylimide or on its pure dichloride, in the presence of benzene and carbon bisulphide, gives very much smaller yields of the body, $C_{26}H_{20}N_4$, than when the reaction is carried out in the presence of approximately *one* equivalent of hydrogen chloride.

Two grams of pure freshly made and freshly distilled carbodiphenylimide were dissolved in benzene and carbon bisulphide, and the solution treated with aluminium chloride in the usual manner. From the reaction-product 0.107 gram (=5½ per cent.) of the body, $C_{26}H_{20}N_4$, was obtained.

Five grams of the pure dihydrochloride of carbodiphenylimide treated, in the presence of benzene and carbon bisulphide, with aluminium chloride in the usual way, gave 0.47 gram (=12½ per cent.) of the yellow body $C_{26}H_{20}N_4$. The theoretical significance of these results has already been discussed.

The molecular weight determination of the α-form of the yellow body, $C_{26}H_{20}N_4$, by the lowering of the freezing-point of benzene, showed the body to have the double formula :

	Benzene. Grams.	Substance. Gram.	Lowering.	Mol. weight. Found.
I.	35.62	0.3356	0.136°	347
	35.62	0.6086	0.240°	356
II.	35.44	0.5494	0.223°	348
	35.44	0.8184	0.335°	354

Calculated for $C_{13}H_{10}N_2$, 194 ; for $C_{26}H_{20}N_4$, 388.

The determination by the elevation of the boiling-point of chloroform,[1] led to the same conclusion :

Chloroform. Grams.	Substance. Gram.	Elevation.	Mol. weight. Found.
28.7	0.6242	0.223°	360
28.7	0.9904	0.344	372

Analysis of the β-form showed that it has the same composition as the α-form :

0.1830 gram of the β-form gave 24.2 cc. N_2 at 26° and 745.5 mm.

	Calculated for $C_{13}H_{10}N_2$ or $C_{26}H_{20}N_4$.	Found.
N	14.44	14.48

The molecular weight determination of the β-form, by the freezing-point method in benzene, also showed the double formula to be the correct one :

Benzene. Grams.	Substance. Gram.	Lowering.	Mol. weight found.
20.3	0.4046	0.271°	368
20.3	0.6701	0.466°	354

The two forms (α and β) are converted into each other with the greatest ease. When the α-form is heated to its melting-point and allowed to cool slowly, it crystallizes in rhombic plates of the β-form, and these when heated again melt sharply at 184°. The α-form dissolves in benzene very readily, but the clear solution soon deposits rhombic plates of the β-form, melting at 184°. Either form, crystallized from any of the following solvents : alcohol, acetone, ligroin, ethyl acetate, acetoacetic ester, acetic anhydride or aniline, gives *only* the α-form. The fact that crystallization from benzene gave one form, while from alcohol the other was obtained, caused a determination of the solubility of each form, in each of these solvents, to be made. At the temperature of the room, a saturated solution in benzene contains :

α-Form (prisms). Per cent.	β-Form (plates). Per cent.
14.2	7.3

A saturated solution in alcohol contains :

[1] Molecular elevation taken as 36.6° : Beckmann : Ztschr. phys. Chem., 8, 227.

α-Form. Per cent.	β-Form. Per cent.
0.17	0.24

The result shows that, in both cases, it is the less soluble form, which crystallizes from the solvent. Finding later that the α-form is obtained by crystallizing from acetone, it was predicted that this form would be less soluble in this solvent. Experiments confirmed this.

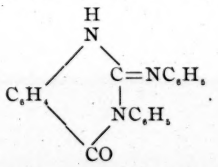
A saturated solution in acetone contains:

	α-Form. Per cent.		β-Form. Per cent.
I.	5.73	III.	6.74
II.	5.89	IV.	7.33

The β-form dissolves in acetone quite readily, but the α-form separates so quickly, that in determination III, this began to take place during the filtration; hence the low result.

The body $C_{24}H_{20}N_4$ is remarkably stable towards heat, distilling unchanged in a vacuum above 340°. The distillate solidifies to an amber-like amorphous mass, which has no definite melting-point, beginning to soften at about 100°. On standing and especially on warming and also by the use of solvents, the amorphous substance is readily converted, according to the conditions, into the α- or β-crystalline form. The results of these experiments led to the conclusion that the two forms are physical or crystallographic modifications of the same substance. On the other hand a most surprising difference was found in the behavior of benzene solutions of the two forms towards phenyl isocyanate, as will be discussed later, a fact which would seem to point to a chemical difference between the two forms.

2-*Phenylimido*-3(N)-*phenyl*-4-*ketotetrahydroquinazoline*,



Both forms of the yellow body, $C_{26}H_{20}N_4$, dissolve in dilute hydrochloric acid, forming a bright yellow solution which becomes perfectly colorless on standing in the cold several hours, or in a few minutes at the boiling-point. Alkalies now precipitate from the colorless solution a white base, which has been shown to be 2-phenylimido-3(N)-phenyl-4-ketotetrahydroquinazoline, $C_{20}H_{15}N_3O$, while aniline remains in the aqueous solution. The aniline was identified, after distilling it off with steam, by the bleaching-powder reaction, by the isonitrile test, and by conversion into benzanilide. The latter melted at 160°, and the melting-point remained unchanged on mixing with pure benzanilide, made in the usual way. The new body is a decided base, dissolving easily in dilute acids, from which alkalies precipitate it unchanged. Recrystallized from alcohol, it is obtained in colorless needles, melting at 163°. It is easily soluble in benzene, chloroform, and carbon bisulphide; less soluble in alcohol and ether, and almost insoluble in low-boiling ligroin and water.

0.1225 gram gave 0.3460 gram CO_2, and 0.0545 gram H_2O.
0.1042 gram gave 12.65 cc. N_2 at 23° and 759.7 mm.

	Calculated for $C_{20}H_{15}N_3O$.	Found.
C	76.62	77.05
H	4.82	4.98
N	13.45	13.75

The reaction has taken place according to the following equation:

$$C_{26}H_{20}N_4 + H_2O \longrightarrow C_{20}H_{15}N_3O + C_6H_5NH_2.$$

A quantitative experiment gave an almost theoretical yield of the body $C_{20}H_{15}N_3O$,—77.9 instead of 80.6 per cent.

The body, $C_{20}H_{15}N_3O$, is saponified but very slowly by boiling with concentrated hydrochloric acid or with alcoholic potash. For the further saponification, 5.3 grams of the substance, with 12 cc. of concentrated hydrochloric acid, was heated in a sealed tube seven hours at 160°–180°. On cooling, large colorless plates (3.1 grams) had formed. These were separated from the brown acid solution, which latter gave with alkali 0.4 gram of the unchanged base. The alka-

line filtrate on extraction with ether gave aniline, which was identified by its boiling-point, 183°, and by the melting-point 160°, of the benzanilide formed by treating it with benzoyl chloride. The melting-point was not changed by mixing with synthetic benzanilide.

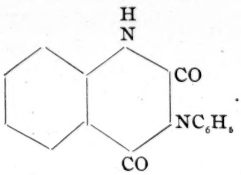
The above-mentioned colorless crystals, after recrystallization from boiling alcohol, formed needles melting at 272°.

0.1849 gram gave 0.4775 gram CO_2, and 0.0718 gram H_2O.

0.1303 gram gave 13.8 cc. N_2 at 16° and 742.1 mm.

	Calculated for $C_{14}H_{10}N_2O_3$.	Found.
C	70.54	70.44
H	4.23	4.34
N	11.79	12.09

The composition and melting-point are those of 2-4-diketo-3(N)-phenyltetrahydroquinazoline,[1]



The analyzed body, like that described by Busch and by Paal, shows in alkaline solution an extraordinary blue fluorescence. The phenomenon is especially beautiful in dilute solution; in stronger solutions in the presence of much alkali it is much fainter. As a complete proof of the identity of the body obtained by me, with that of Busch and Paal, the body was made according to the directions of the latter from anthranilic acid and phenyl isocyanate. By mixing the quinazoline bodies obtained in both ways the melting-point (273°) remained unchanged; all other properties were also identical. Hence it follows that the saponification has taken place thus:

$$C_{20}H_{18}N_2O + H_2O \longrightarrow C_{14}H_{10}N_2O_3 + C_6H_5NH_2.$$

The method of synthesis and its properties leave no doubt

[1] Busch: J. prakt. Chem. [2], **51**, 265; Paal: Ber. d. chem. Ges., **27**, 978.

concerning the constitution of 2-4-diketotetrahydroquinazoline—the body $C_{14}H_{10}N_2O_2$. The constitution of the body, $C_{20}H_{18}N_2O$, must therefore be represented by one of the formulas I*a*, I*b*, II or III, page 134. As has already been mentioned, formula III is excluded by the properties of the body, while, between I(*a* or *b*) and II, the former was given the preference and the constitution proved by preparing such a compound synthetically. It was found to be identical with the base $C_{20}H_{18}H_2O$. The first step in the synthesis was the preparation of

2-Thio-3(N)-phenyl-4-ketotetrahydroquinazoline,

$$C_6H_5—N—CO—C_6H_4—NH—C=S.$$

Anthranilic acid (10 grams) was dissolved in 100 cc. of alcohol and 50 cc. of water, containing a little over one molecule of potassic hydrate, and phenyl mustard-oil (9 grams = 1 mol.) added. Most of the mustard-oil goes into solution at once. After standing two or three hours, with occasional shaking, the reaction is complete. Without alcohol the action is extremely slow, but with an excess of alcohol much phenylthiourethane is formed. Water is added after the reaction is complete. The solution is filtered from a small oily precipitate, when necessary, and saturated with carbon dioxide. The nearly white heavy granular precipitate, which forms very slowly, is complete only after several hours. For further purification the product was dissolved in dilute alkali and again treated with carbon dioxide, which now causes a rapid separation of a voluminous precipitate.

By its analysis and behavior, the body was shown to be the above-mentioned thioquinazoline.[1] It is a very weak acid, like all similar thioamides; it dissolves in alkalies (without fluorescence), and is then precipitated immediately by carbon dioxide; it is difficultly soluble in most organic solvents, and crystallizes from a mixture of alcohol and acetone in almost colorless rectangular plates, which melt without decomposition above 300°.

0.1540 gram gave 15.7 cc. N_2 at 23° and 748.7 mm.

[1] *Vide* Stewart: J. prakt. Chem. [2], 49, 415.

	Calculated for $C_{14}H_{10}N_2SO$.	Found.
N	11.05	11.38

In the action of phenyl mustard-oil on anthranilic acid, the first product is evidently *o*-phenylthioureïdobenzoic acid:

$$NH_2C_6H_4COOK + C_6H_5N{=}CS \longrightarrow C_6H_5NHCS{-}NHC_6H_4{-}COOK.$$

The latter is stable in alkaline solution, but in the small quantity in which it is liberated in the solution by the weaker carbonic acid, it loses water, forming the quinazoline derivative:

$$C_6H_5NHCS{-}NHC_6H_4COOH \longrightarrow C_6H_5{-}N{-}CO{-}C_6H_4{-}NH{-}C{=}S + H_2O.$$

The formation of 2-4-diketo-3(N)-phenyltetrahydroquinazoline, by evaporating a solution of the ammonium salt of phenylureïdobenzoic acid,[1] must depend in a similar manner upon the gradual liberation of the acid by the slow decomposition of the salt in solution. The intermediate thioureïdobenzoic acid may be isolated by treating the reaction-product of anthranilic acid and mustard-oil, with hydrochloric acid instead of carbonic acid. This causes an immediate precipitate, which contains some quinazoline. To remove the latter the precipitate is dissolved in aqueous sodium bicarbonate, in which the quinazoline is insoluble, quickly filtered, and again precipitated with hydrochloric acid. The thioureïdo acid so prepared, after being dried on a clay plate, was crystallized by dissolving in acetone and adding ligroin (40°–60°). The colorless needles are undoubtedly *o*-phenylthioureïdobenzoic acid. The acid melts with decomposition at 185°–190°, when plunged into the hot bath. It is readily soluble in sodium bicarbonate, and on treating the solution with carbon dioxide the thioquinazoline slowly separates out as before.

By oxidation with potassium permanganate Busch[2] converted 2-thiotetrahydroquinazoline into 2-4-diketotetrahydroquinazoline. Similarly, 2-thio-3(N)-phenyl-4-ketotetrahy-

[1] Paal: *Loc. cit.* [2] J. prakt. Chem. [2], **51**, 128.

droquinazoline is readily oxidized to 2-4-diketo-3(N)-phenyltetrahydroquinazoline; 5 grams of the thio-body were heated to about 90° with 400 cc. of water, and the calculated amount (8.5 grams) of potassium permanganate added slowly. The oxidation is complete in half an hour. Any excess of permanganate is destroyed by alcohol, sufficient alkali is added to dissolve all the diketone, and the manganese dioxide filtered out. With acids the colorless filtrate gives almost pure 2-4-diketo-3(N)-phenyltetrahydroquinazoline. This method is, in fact, very convenient for preparing the diketoquinazoline, and dispenses with the use of phenyl isocyanate which is not readily obtained nor easily preserved unchanged.

The synthesis of 2-phenylimido-3(N)-phenyl-4-ketotetrahydroquinazoline was accomplished by

The Action of Aniline on 2-Thio-3(N)-phenyl-4-ketotrahydroquinazoline.

Aniline acts on the thioquinazoline with great difficulty; neither by boiling with aniline in an open vessel, nor by heating with aniline hydrochloride could the reaction, which usually takes place with other thioanilides, be made to give even a fair yield of the desired product. One gram of the thio-body was heated with 5 grams of aniline in a sealed tube at 300° for several hours. Hydrogen sulphide escaped on opening the tube. On treating the residue with hydrochloric acid a portion dissolved, and the highly diluted acid solution gave, with alkali, a light-colored precipitate, which after repeated recrystallization gave a small amount of light-yellowish needles, melting at 161°.5. Pure 2-phenylimido-3(N)-phenyl-4-ketotetrahydroquinazoline is colorless and melts at 163°; but, as a mixture of the synthetic needles with the pure analyzed quinazoline compound melted at 162°, the identity of the two cannot be doubted. Hence the following reaction takes place to a certain, though slight, extent:

$$C_6H_5—N—CO—C_6H_4—NHC=S + C_6H_4NH_2 \rightarrow$$

$$C_6H_5—N—CO—C_6H_4—NH—C=NC_6H_5.$$

Since in the thio-body the sulphur atom is in position 2, it follows that the aniline group is also in 2 and not in 4; that, therefore, formula I(*a* or *b*), page 134, must represent the body $C_{20}H_{15}N_3O$.

As the thio-ethers[1] of thioanilides are especially reactive toward aniline, the ethyl ether of the above thio-body was made and treated with aniline, in the hope of obtaining a better yield of the body, $C_{20}H_{15}N_3O$, synthetically.

2-Ethylthio-3(N)-phenyl-4-ketodihydroquinazoline,

$$C_6H_5—N—CO—C_6H_4—N=C—SC_2H_5.$$

2-Thio-3(N)-phenyl-4-ketotetrahydroquinazoline was covered with alcohol, brought into solution by 30 per cent. potassic hydrate, and somewhat more than the calculated amount of ethyl iodide added. The solution after boiling half an hour and filtering from a slight residue gave, on cooling, long colorless needles of the thio-ether, the amount of which was increased to an almost theoretical yield by evaporating the mother-liquor. After a crystallization from somewhat dilute alcohol the substance is pure. It forms long, colorless needles melting at 114°. By boiling with dilute hydrochloric acid, ethylmercaptan (recognized by its odor) was given off, and the residue gave, with dilute alkali, a solution having the characteristic violet fluorescence of 2-4-diketo-3(N)-phenyltetrahydroquinazoline:

$$C_6H_5.N.CO.C_6H_4.N:C—SC_2H_5 + H_2O \rightarrow$$

$$C_6H_5—N—CO.C_6H_4—NH.CO + C_2H_5SH.$$

The method of preparation and the behavior with hydrochloric acid show that the body has the constitution given.

0.1592 gram gave 14.25 cc. N_2 at 24° and 748 mm.

	Calculated for $C_{14}H_{14}N_2SO$.	Found.
N	9.95	9.93

As a further means of confirming the constitution of my

[1] Wallach: Ber. d. chem. Ges., **12**, 1061.

thio-ether,[1] I have also made the corresponding methyl ether, $C_6H_5—N(—CO.C_6H_4.N : C—SCH_3)$, in exactly the same way as that by which the ethyl ether was obtained. It forms long needles melting at 125°, easily soluble in alcohol.

0.1032 gram gave 0.0888 gram $BaSO_4$.

	Calculated for $C_{18}H_{12}N_2SO$.	Found.
S	11.94	11.83

Boiled with dilute hydrochloric acid it is slowly saponified, giving methylmercaptan and leaving the diketoquinazoline. The isomeric 1(N)-methyl body, 1(N)-methyl-2-thio-3(N)-phenyl-4 ketotetrahydroquinazoline,

$$C_6H_5—N(—CO.C_6H_4—NCH_3—C=S),$$

has recently been made by Fortmann,[2] from methylanthranilic acid, and melts at 288°–289°. There can therefore be no doubt as to the nature of the thio-ether obtained by me.

The Action of Aniline on 2-Ethylthio-3(N)-phenyl-4-ketodihydroquinazoline.

To accomplish a reaction with aniline 2-ethylthio-3(N)-phenyl-4-ketodihydroquinazoline must be heated in a sealed tube. 1 gram of the ether was heated to 300° for eight hours with 5 grams of aniline. On opening the tube the odor of mercaptan was very strong. After distilling off the excess of aniline, the larger part of the dark-red residue dissolved in hot dilute hydrochloric acid, forming a dark-green solution. By fractional precipitation with alkali a small amount of a dark-red mass was obtained which contains a dye that dissolves in alcohol forming a red solution, having a remarkable orange-colored fluorescence. Acids change the color to green. The dye has not yet been studied further. From the principal part of the precipitate with alkali, after decolorizing by boiling the alcoholic solution with animal charcoal, nearly colorless needles melting at 162°.5 were obtained; these mixed with pure 2-phenylimido-3(N)-phenyl-4-ketotetrahydroquin-

[1] *Vide* Ber. d. chem. Ges., **30**, 1690. [2] J. prakt. Chem., **55**, 132.

azoline (m. p. 163°) showed the same melting-point. The reaction,

$$C_6H_5—N—CO—C_6H_4—N=C—SC_2H_5 + C_6H_5NH_2 \longrightarrow$$
$$C_6H_5.N.CO.C_6H_4.NH.C=NC_6H_5 + C_2H_5SH,$$

has therefore occurred. The yield, about 10 per cent., was somewhat better than in the preceding synthesis, but still unsatisfactory.

The idea suggested itself that, by replacing sulphur in 2-thio-3(N)-phenyl-4-ketotetrahydroquinazoline by chlorine, a body could be obtained that would react readily and smoothly with aniline to give the body $C_{20}H_{15}N_3O$. Such proved to be the case. By exactly the same method as that by which chlormethenylaminophenol was obtained[1] from thiocarbaminophenol, the above thioquinazoline derivative yields the corresponding chloride.[2]

2-Chlor-3(N)-phenyl-4-ketodihydroquinazoline,
$C_6H_5.N.CO.C_6H_4.N=CCl.$

Five grams of the dry, finely powdered thio-body were suspended in 50 grams of dry chloroform, free from alcohol, and treated with carefully dried chlorine. The mixture warmed somewhat, but even with an excess of chlorine a large amount of a yellow body remained undissolved. The mixture was poured into water in small quantities and shaken vigorously, thus destroying the chloride of sulphur and causing the yellowish body to dissolve in the chloroform. After washing with dilute alkali and with water, and drying the chloroform solution with calcium chloride, the solvent was distilled off leaving the chlorquinazoline as a light-colored oil which soon crystallized in needles. The crystals, after washing with ether and drying, melt at 130°, but are not quite pure. For the analysis the body was distilled in a vacuum. It boils at about 245° at 15 mm. and the distillate forms a pure, white, crystalline mass, melting at 131°.5. It is easily

[1] *Vide*, p. 123.

[2] Cf. Gabriel: Ber. d. chem. Ges., 29, 1306.

soluble in chloroform and benzene, less in alcohol and ether, and difficultly soluble in ligroin (40°–60°). From a solution in benzene the body is precipitated by ligroin in needles. It may be recrystallized from boiling alcohol unchanged,—a fact which shows how firmly the chlorine atom is held in the molecule.

An attempt to determine the chlorine according to Carius was unsuccessful. After heating for six hours at 240° and for four hours at 340° a considerable amount of an orange-colored compound, insoluble in acids, remained unoxidized. A chlorine determination was easily accomplished in a very short time by boiling, for thirty minutes, a solution of the weighed substance with 20 cc. of pure methyl alcohol in which 0.5 gram of sodium had been dissolved. The solution, from which common salt had separated, was diluted with water, acidified with nitric acid, and titrated with silver nitrate, according to Volhard.

0.1863 gram required 7.35 cc. $\frac{N}{10}$ $AgNO_3$.

0.4260 gram required 16.53 cc. $\frac{N}{10}$ $AgNO_3$.

	Calculated for $C_{14}H_9N_3ClO$.	Found. I.	II.
Cl	13.84	13.79	14.00

2-Dichlor-3(N)-phenyl-4-ketotetrahydroquinazoline,

$C_6H_5.N.CO.C_6H_4.NH.C.Cl_2$.

Like chlormethenylaminophenol, the above analyzed monochlorquinazoline gives, with dry hydrogen chloride, a dichloride, which in all probability is to be represented by the above formula. Carefully dried hydrogen chloride was passed into a solution of 2-chlor-3(N)-phenyl-4-ketodihydroquinazoline in benzene. A white precipitate resulted which, after filtering and washing with ligroin as quickly as possible, was pressed on a clay plate for a minute or so and then dried in a vacuum over sulphuric acid. On opening the desiccator, a very little hydrochloric acid was noticed, showing slight decomposition. The substance melts at 140° with decomposition. In contact with water, it readily loses one molecule of acid, giving the original quinazoline chloride.

For the analysis the weighed substance was covered with water and titrated with alkali, methyl orange being used as an indicator.

0.2901 gram required 9.6 cc. $\frac{N}{10}$ alkali.
0.2800 gram required 9.0 cc. $\frac{N}{10}$ alkali.

	Calculated for $C_{14}H_9N_3ClO.HCl$.	Found. I.	II.
Cl	12.09	11.73	11.40

In the preparation of 2-chlor-3(N)-phenyl-4-ketodihydroquinazoline from the thio-derivative, the yellowish body insoluble in chloroform remaining after the treatment with chlorine is undoubtedly the above dichloride.

Synthesis of 2-Phenylimido-3(N)phenyl-4-ketotetrahydroquinazoline.

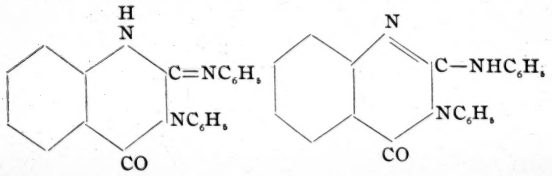
2-Chlor-3(N)-phenyl-4-ketodihydroquinazoline dissolves readily in aniline, but the reaction with it goes on very slowly in the cold; only after two days had the mixture solidified. At the boiling-point of aniline the reaction is complete in fifteen minutes; on cooling the product solidifies to a crystalline mass, which dissolves readily in aqueous hydrochloric acid, with the exception of a small dark-colored residue. The nearly colorless filtrate gives with alkalies an almost white precipitate which, after recrystallization from alcohol, forms colorless needles melting at 163°. The body thus obtained was identical in every respect with 2-phenylimido-3(N)-phenyl-4-ketotetrahydroquinazoline,

$$C_6H_5—N—CO—C_6H_4—NH—C = NC_6H_5,$$

obtained by the saponification of the yellow base, $C_{26}H_{20}N_4$, which is formed by the Friedel and Crafts reaction from the hydrochloride of carbodiphenylimide. When the substances made in both ways are mixed there is no change in the melting-point. Thus the absolute identity of the substances is established. The new method of preparing 2-phenylimido-3(N)-phenyl-4-ketotetrahydroquinazoline is much to be preferred to the old, as the yields in all of the transformations are

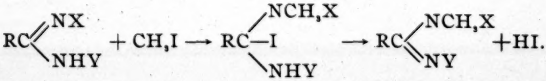
excellent. A large part of the substance used was prepared in this way.

This synthesis confirms the constitution already established by the other two syntheses from the thio-derivatives. The body, $C_{20}H_{18}N_4O$, has, therefore, one of the so-called tautomeric forms *a* or *b*:



a. *b.*

The question still remained: Which of these two formulas is to be ascribed to the body in hand? The question is very much like that concerning the constitution of the amidines, the diazoamido bodies, etc. Of all these analogous bodies, experiment has shown that, with a very few doubtful exceptions, but one of the two possible forms exists. In his work on amidines, von Pechmann[1] has used the reaction with methyl iodide to determine the position of the "labile" hydrogen atom, assuming that the methyl group takes the place occupied by the hydrogen atom. This method is, however, not entirely free from objection, since it is possible that the methyl iodide may first be added to the double bond, just as hydrogen haloid is added to the double bond of the similarly constituted imido-esters; the loss of hydriodic acid would then give a body having the methyl attached to the nitrogen atom which originally held no hydrogen; thus,



Direct substitution of methyl for hydrogen would give

[1] Ber. d. chem. Ges., **28**, 869, 2362.

. The same amidine could thus give two isomeric methyl derivatives; in fact where X and Y are very similar, two alkyl derivatives are obtained by treating with alkyl iodide. The results of the action of methyl iodide admit of an ambiguous interpretation when viewed from the standpoint of Nef.[1] Here, besides the absorption of the amidine by methylene, an addition of hydrogen iodide to the double bond of the amidine may first take place leading to a rearranged product.

In the case of the diazoamido bodies H. Goldschmidt[2] has employed a reagent for determining the constitution with which the possibility of a rearrangement is excluded, namely, phenyl isocyanate, his leading thought being that, in reactions with phenyl isocyanate, all traces of moisture, acids, etc., can be excluded, which could cause the change of one form of these closely allied "tautomeric" substances into the other. Further, phenyl isocyanate cannot be absorbed by a double bond of the body whose constitution is to be determined; on the contrary, the only possible reaction is an absorption of the latter body by the isocyanate, giving a urea derivative, the determination of whose constitution fixes that of the compound in question. This excellent reagent was applied in the present investigation with the view of deciding between the two possible formulas *a* and *b* (p. 154) for the body $C_{20}H_{18}N_2O$.

The Action of Phenyl Isocyanate on 2-Phenylimido-3(N)-phenyl-4-ketotetrahydroquinazoline.

The substances do not act readily in the cold nor by heating at 150° for one hour. The desired reaction took place, however, when 7 grams of the body $C_{20}H_{18}N_2O$ were dissolved in 80 cc. of dry benzene containing 2.6 grams of phenyl isocyanate and allowed to stand for eleven days in a well-corked flask placed in a desiccator which was kept in a light place. The solution, which had become somewhat brown, was treated with alcohol to convert the unchanged cyanate into easily soluble urethane, since by exposure to the air the

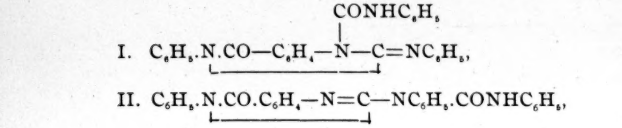
[1] Ann. Chem. (Liebig), **298**, 202. [2] Ber. d. chem. Ges., **21**, 2557.

cyanate would absorb water with the formation of carbanilide, which would be difficult to remove. The benzene was distilled off in a vacuum and the viscous residue dissolved in 60–70 cc. of hot alcohol. From the brown solution a large amount of colorless crystals separated on cooling. These consist of a mixture of the unchanged basic body, $C_{20}H_{18}N_2O$, and the new urea. To remove the former the mixture was treated with dilute hydrochloric acid. The neutral insoluble residue by recrystallization from hot alcohol gave 3.2 grams of colorless needles, melting at 127°. According to its behavior and its analysis, the new substance is the expected urea.

0.1099 gram gave 13.2 cc. N_2 at 23° and 742.2 mm.

	Calculated for $C_{27}H_{20}N_4O_2$.	Found.
N	12.96	13.28

The urea must have either the constitution I. or II.



corresponding to the formulas *a* and *b* (page 154) respectively, for the body $C_{20}H_{18}N_2O$.

By heating to 130° the urea is completely decomposed into phenyl isocyanate and the body $C_{20}H_{18}N_2O$. The latter, after removing the cyanate in a current of air, was perfectly pure, and formed a white crystalline mass, having the correct melting-point, 163°. Its identification was established by mixing with the pure substance, when the melting-point remained unchanged.

It was hoped that a urea of constitution II could be prepared by the following method, which would leave no doubt of its constitution, but all attempts were unsuccessful. 2-Chlor-3(N)-phenyl-4-ketodihydroquinazoline and ethylisodiphenylurea[1] should react[2] to give a body of constitution II:

[1] Lengfeld and Stieglitz: Ber. d. chem. Ges., **27**, 926.

[2] *Vide* paper by Dains soon to be published in The Journal of the American Chemical Society.

$$C_6H_5.N.CO.C_6H_4.N{=}CCl + C_6H_5NHC(OC_2H_5) : NC_6H_5 \longrightarrow$$
$$C_6H_5.N.CO.C_6H_4.N{=}C{-}NC_6H_5CONHC_6H_5 + C_2H_5Cl.$$

The two substances were fused together, but no apparent action took place below 230°; from 230° to 260° a gas was given off which, by its burning with a green-bordered flame, was identified as ethyl chloride. Oily drops condensed on the walls of the upper portion of the tube; these had the powerful, unmistakable odor of phenyl isocyanate. From the dark residue no urea of the nature expected could be isolated. From the fact that ethyl chloride and isocyanate are formed, it is probable that the reaction takes place in the manner predicted; but the complex urea formed, whether I or II, is unstable at the temperature of the reaction and breaks down into isocyanate and the body $C_{20}H_{15}N_3O$, exactly as the urea above described is completely decomposed at 130°, giving just these products. This view is further supported by the fact that ethylisodiphenylurea alone gives no odor of isocyanate when heated; the isocyanate observed in the reaction must therefore come from the decomposition of an unstable urea.

As the pure chloride and urea ether react only far above the decomposition-point of the urea expected, equal molecules of the quinazoline chloride and ethylisodiphenylurea were dissolved in dry benzene and boiled together for twenty hours, but no reaction took place.

These attempts to determine the constitution of the body $C_{20}H_{15}N_3O$ having failed, owing to the unusual difficulty with which the chlorine in 2-chlor-3(N)-phenyl-4-ketodihydroquinazoline enters into reaction, recourse was had to von Pechmann's methylation method for distinguishing closely allied amidines. This method, while less reliable, perhaps, led to a definite result, the methyl group going into position 1; in accordance with this the urea just described would have the constitution represented by formula I, p. 156.

The Action of Methyl Iodide on 2-Phenylimido-3(N)-phenyl-4-ketotetrahydroquinazoline.

Two grams of the quinazoline and 20 grams of methyl

iodide, in which the quinazoline is easily soluble, were heated in a sealed tube to 100° for nine hours. The brown product was partly insoluble in the excess of methyl iodide. The latter was distilled off, and the residue dissolved in pure acetone, in which it is easily soluble. The acetone solution was treated with aqueous hydrochloric acid and much water added. A brick-red tar separated in small quantity, leaving a colorless solution of the bases, which were precipitated fractionally by alkali. After one crystallization from alcohol, the first fraction was the nearly pure unmethylated white base, $C_{20}H_{18}N_2O$, as was shown by its melting-point (162°), which changed to 162°.5 by mixing with some of the pure body, $C_{20}H_{18}N_2O$ (m. p. 163°). The second fractional precipitate with alkali, after one crystallization from alcohol, melted at 135°–140°, and was evidently a mixture. The third fraction, which was small, after recrystallization from alcohol, melted at 174°. The new body, which was found to be the methyl derivative of the white base, $C_{21}H_{18}N_2O$, forms colorless needles melting at 174°, easily soluble in alcohol. The perfectly pure substance amounted to but 0.05 gram, but the experiment was not repeated to obtain sufficient for an analysis, as the constitution could be firmly established only by the saponification products. The two possible reactions are represented by :

$$\text{I. } C_6H_5.\underbrace{N.CO.C_6H_4.NCH_2.C}=NC_6H_5 + H_2O \longrightarrow$$

$$C_6H_5.\underbrace{N.CO.C_6H_4.NCH_2.C}=O + C_6H_5NH_2;$$

$$\text{and II. } C_6H_5.\underbrace{N.CO.C_6H_4.N}:C.NCH_3.C_6H_5 + H_2O \longrightarrow$$

$$C_6H_5.\underbrace{N.CO.C_6H_4.NHCO} + C_6H_5NHCH_3.$$

It was finally established that the products of saponification are those given by reaction I.—aniline and 1(N)-methyl-2-4-diketo-3(N)-phenyltetrahydroquinazoline. The base melting at 174° produced by methylation of the white base (m. p. 163°) must therefore be 1(N)-methyl-2-phenylimido-3(N)-phenyl-4-ketotetrahydroquinazoline, and the white base itself

(m.p. 163°) is accordingly 2-phenylimido-3(N)-phenyl-4-keto-tetrahydroquinazoline.

The methylated body (m. p. 174°) was heated in a sealed tube with concentrated hydrochloric acid to about 180° for four hours. The product consisted of light-colored needles, insoluble in the acid. Water was added and the crystals filtered off. The filtrate gave no precipitate with alkali, showing the saponification to have been complete. The crystals are insoluble in dilute acids and alkalies, somewhat soluble in hot concentrated hydrochloric acid, and crystallize out on cooling. The crude saponification-product melted at 222°, and after dissolving in benzene and precipitating with ligroin (40°–60°), when the substance was obtained in nearly white needles, the melting-point was 223°. 2-4-Diketo-3(N)-phenyltetrahydroquinazoline, the product to be expected, if equation II, page 158, represented the saponification reaction, melts at 272° and is soluble in alkali. It was therefore thought that the substance melting at 223° must be its 1-methyl derivative, 1(N)–methyl–2-4–diketo-3(N)–phenyltetrahydroquinazoline, the saponification-product to be expected according to equation I. This substance had, however, been prepared by Fortmann[1] from methylanthranilic acid and phenyl isocyanate, and he gives the melting-point at 233°. In all other respects the body obtained by me and melting at 223° showed the behavior of Fortmann's body. To settle the question, raised by this discrepancy in melting-point, I prepared the same substance by methylating 2-4-diketo-3(N)-phenyltetrahydroquinazoline, in alkaline solution, according to

$$C_6H_4.N.CO.C_6H_4.NH.CO + CH_3I \longrightarrow$$

$$C_6H_4.N.CO.C_6H_4.NCH_3.CO + HI.$$

1(N)-*Methyl-2-4-diketo-3(N)-phenyltetrahydroquinazoline*, $C_6H_4.N.CO.C_6H_4.NCH_3.CO$.

Two grams of 2-4-diketo-3(N)-phenyltetrahydroquinazoline, dissolved in 65 cc. of methyl alcohol, containing 18 cc.

[1] J. prakt. Chem. [2], **55**, 130.

(1 mol.) of $\frac{N}{2}$-potassic hydrate was boiled with 5 to 6 grams of methyl iodide for one hour. On cooling, colorless needles separated in considerable quantity. The substance was recrystallized from alcohol containing a little aqueous alkali, to remove any unchanged diketone. After two more crystallizations from pure alcohol, colorless needles, melting at 224°, were obtained; neither by further recrystallization from alcohol nor by dissolving in benzene and precipitating with ligroin could the melting-point be raised above 224°. An analysis proved the purity of the substance.

0.2045 gram gave 0.5339 gram CO_2, and 0.0866 gram H_2O.

	Calculated for $C_{16}H_{12}N_2O_2$.	Found.
C	71.43	71.22
H	4.76	4.74

The body is therefore 1(N)-methyl-2-4-diketo-3(N)-phenyltetrahydroquinazoline. In all particulars, excepting melting-point, it agrees with that of Fortmann. It is insoluble in both acids and alkalies; it has further the exact properties of the methyl body obtained by the saponification of the methylation-product of the body $C_{20}H_{18}N_2O$. This was very faintly colored, and melted at 223° (instead of 224°), and a mixture with the pure analyzed body melted at 223°–224°, showing the identity of the two.[1]

To remove the last possible doubt that the body obtained by methylating 2-4-diketo-3(N)-phenyltetrahydroquinazoline in alkaline solution is really the (N)-methyl derivative and not the oxymethyl ether, 2-methoxy-3(N)-phenyl-4-ketodihydroquinazoline, $C_6H_4{<}\begin{matrix}N\text{—}CO.C_6H_4\text{—}N{=}C.OCH_3\\ \text{└——————————┘}\end{matrix}$, this latter was prepared.

2-Methoxy-3(N)-phenyl-4-ketodihydroquinazoline, $C_6H_4{<}\begin{matrix}N\text{—}CO.C_6H_4\text{—}N{=}C.OCH_3\\ \text{└——————————┘}\end{matrix}$.

The above oxy-ether was made by heating 2-chlor-3(N)-

[1] I can assign no reason for the difference of 9° between the melting-point of 1(N)-methyl-2-4-diketo-3(N)-phenyltetrahydroquinazoline found by Fortmann and that found by myself. As I obtained the substance by two entirely independent methods, I am inclined to think that the lower melting-point, found by me, is the correct one, and that Fortmann's value may be due to a typographical error, 233° being given for 223°.

phenyl-4-ketodihydroquinazoline with sodium methylate in methyl alcohol, according to

$$C_6H_5.N.CO.C_6H_4—N=CCl + NaOCH_3 \longrightarrow$$
$$C_6H_5.N.CO.C_6H_4.N=C.OCH_3 + NaCl.$$

After filtering off the common salt formed and adding a little water, colorless crystals separated, which, after crystallization from methyl alcohol formed, apparently, rhombohedrons melting at 134°. The chloride used melts at 133°, but the new substance contained no chlorine, and a mixture with the chloride showed a strong depression of the melting-point (to about 110°) as expected. The new body dissolves in concentrated hydrochloric acid and, on warming, a gas which burned with a green-bordered flame (methyl chloride) was given off, while a white insoluble crystalline precipitate was formed. The latter dissolved in dilute alkali, with a blue fluorescence, and was undoubtedly 2-4-diketo-3(N)-phenyltetrahydroquinazoline, formed according to the equation :

$$C_6H_5—N—CO.C_6H_4.N=COCH_3 + HCl \longrightarrow$$
$$C_6H_5.N.CO.C_6H_4.NH.CO + CH_3Cl.$$

The method of synthesis and the behavior with hydrochloric acid leave no doubt that this new ether (m. p. 134°) is the oxygen ether of 2-4-diketo-3(N)-phenyltetrahydroquinazoline ; the isomeric ether (m. p. 224°) obtained by methylating the diketone in alkaline solution must therefore be the nitrogen ether, 1(N)-methyl-2-4-diketo-3(N)-phenyltetrahydroquinazoline, $C_6H_5.N.CO.C_6H_4.NCH_3.CO$, which is in accord with the behavior of all analogous alkali salts of acid amides when subjected to methylation. The methoxy derivative was not analyzed.

Since 1-(N)-methyl-2-4-diketo-3(N)-phenyltetrahydroquinazoline, together with aniline, is obtained by the saponification of the methylation-product of the body, $C_{20}H_{18}N_2O$, as represented by equation I, p. 158, the latter methyl body

(m.p. 174°) must be 1(N)-methyl-2-phenylimido-3(N)-phenyl-4-ketotetrahydroquinazoline, $C_6H_5.N.CO.C_6H_4.NCH_3.C=NC_6H_5$.

The above proof of the constitution of the methyl derivative just discussed was fully confirmed by preparing synthetically the only other isomeric methyl derivative that could possibly be obtained by methylating a base of the constitution *a* or *b* (p. 154); *viz.*, 2-methylanilido-3(N)-phenyl-4-ketodihydroquinazoline.

2-Methylanilido-3(N)-phenyl-4-ketodihydroquinazoline,

$$C_6H_5—N—CO—C_6H_4—N=C—N(CH_3)C_6H_5.$$

2-Chlor-3(N)-phenyl-4-ketodihydroquinazoline was heated with pure, dry, freshly distilled monomethylaniline to 180° for two hours. The viscous product was treated with hydrochloric acid, in which it dissolved; but very soon a heavy white precipitate, which may have been the hydrochloride of the new base, separated. This was filtered off and dissolved in dilute acid, and precipitated by alkali. By dissolving the free base in methyl alcohol and adding water slowly the body separates in nearly colorless needles, which are very soluble in ethyl and methyl alcohol, less in ether, almost insoluble in low-boiling ligroin, and insoluble in water. The body is a base, being readily soluble in acids and precipitated unchanged by alkalies. For the analysis the body was crystallized from ether by the addition of ligroin, and partial evaporation in a vacuum, and so obtained in colorless needles, melting at 123°.

0.1002 gram gave 11.7 cc. N_2 at 19° and 733.7 mm.

	Calculated for $C_{21}H_{17}N_3O$.	Found.
N	12.84	13.24

Not a particle of this low-melting methyl derivative was obtained by treating the white base,

$$C_6H_5—N—CO—C_6H_4—NH—C=NC_6H_5,$$

with methyl iodide; the sole methylated derivative was proved to be 1(N)-methyl-2-phenylimido-3(N)-phenyl-4-ketotetra-

hydroquinazoline (m. p. 174°). If the supposition be correct that, by the action of methyl iodide on the body, $C_{20}H_{18}N_3O$, the methyl group has taken the position formerly occupied by the "labile" hydrogen atom, it follows that the body, $C_{20}H_{18}N_3O$, has the constitution (*a*) page 154. Assuming this to be the case, the body has been named accordingly; though as has been pointed out, this assumption is not yet entirely free from objection, and the possibility that (*b*), page 154, is by no means absolutely excluded.

The preparation of the two isomeric methyl derivatives of the above base, $C_{20}H_{18}N_3O$, was carried out with the further object of discovering, if possible, whether the remarkable change of color, when the yellow body, $C_{26}H_{20}N_4$, is converted by saponification by acids into the colorless one, $C_{20}H_{18}N_3O$, is due to a shifting of the "labile" hydrogen atom giving rise to the isomeric form. The fact that both of the methyl derivatives of the body, $C_{20}H_{18}N_3O$, are colorless shows that the isomeric form of the original body, if it could exist, would also be colorless; so that the color of the yellow body, $C_{26}H_{20}N_4$, is evidently not due to either possible arrangement of the guanidine group of the molecule. The cause of the color must be intimately connected with the 4-phenylimido group, since when this is removed the body becomes colorless.

Synthesis of 2-4-*Phenylimido*-3(N)-*phenyl*-4-*ketotetrahydroquinazoline* (*The Yellow Base*, $C_{26}H_{20}N_4$),

$$C_6H_5.N.C(:N—C_6H_5).C_6H_4.NH—C=NC_6H_5.$$

One gram of 2-chlor-3(N)-phenyl-4-ketodihydroquinazoline and 0.9 gram of phosphorus pentachloride were dissolved in 5 cc. of phosphorus oxychloride and boiled for ten minutes. No evolution of hydrogen chloride was noted, which was good evidence that chlorination of the benzene rings had not taken place. After distilling off the phosphorus oxychloride the remaining brown oil was mixed directly with about 5 grams of aniline. The reaction took place at once, the mixture became hot, and, on cooling, crystals of aniline hydrochloride separated out. An oil was separated from the crystals by taking up in chloroform and, after removing the solvent, the

oil was boiled for ten minutes with more aniline. On distilling off the aniline, a dark-colored, viscous mass remained. This distilled in a vacuum, with apparently little decomposition, giving a solid yellow distillate, which was dissolved in benzene and the latter partly evaporated. Upon the addition of alcohol a small amount of the characteristic yellow prismatic needles of 2-4-diphenylimido-3(N)-phenyltetrahydroquinazoline ($C_{26}H_{20}N_4$) soon separated out. After recrystallization from alcohol the needles were almost pure and showed the melting-point 170°–171° (instead of 171°). On cooling, the substance crystallized in the melting-tube, and on reheating melted at 182°–183° (instead of 184°), showing thus the exact behavior of the yellow body, $C_{26}H_{20}N_4$, obtained from carbodiphenylimide.

An addition of the α-form (prisms, melting-point 171°) of the body obtained from carbodiphenylimide to the substance made synthetically, did not change the melting-point.

It was of great interest to determine, if possible, the cause of the difference between the α- and β-forms of the yellow body $C_{26}H_{20}N_4$. When it was found, from a solution of either of the two forms, that one was obtained which was the less soluble in the solvent used,[1] it was thought that the two forms must be physical or crystallographic modifications of the same substance, and consequently identical in solution, and thus show in solution the same chemical behavior. In endeavoring to determine the position of the hydrogen atom in the yellow bases (*a* and *b*, p. 136) by converting into the urea by means of phenyl isocyanate, and saponifying to the white urea whose constitution has been fairly well established by the methylation process just discussed, the surprising discovery was made that the α- and β-forms do not seem to act alike in solution. This discovery has been made so recently that the investigation has not been completed, but the point seems so interesting that a brief statement of the facts thus far established will be made now.

The Action of Phenyl Isocyanate on the Yellow Bases, $C_{26}H_{20}N_4$.

The substances react with great difficulty if cold, and heat-

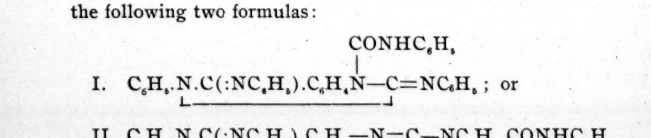
[1] *Vide* p. 143.

ing is not effective, as was the case in the formation of the urea of the body $C_{20}H_{18}N_2O$. To accomplish the reaction I proceeded as follows: 2 grams of the α-form (m. p. 171°) of the body, $C_{26}H_{30}N_4$, and 1.3 grams of phenyl isocyanate (about double the calculated amount) were dissolved in 100 cc. of pure dry benzene, which was much more than enough to prevent the separation of any of the β-form, and the solution allowed to stand in a well-stoppered bottle, exposed to as much sunlight as possible, for three weeks. At the end of this time the solution remained clear and no crystals had separated. The solution was treated with 1 cc. of alcohol, to destroy the excess of cyanate, and most of the benzene distilled off in a vacuum, the temperature being kept below 24°. The concentrated solution thus obtained gave, with alcohol, a precipitate of perhaps a gram of the nearly pure unchanged body, $C_{26}H_{30}N_4$, melting at 170°, instead of 171°. The mother-liquor, on further evaporation in a vacuum at not over 24°, gave a quantity of light-yellow crystals, which melt at 80°–90°, and on heating give off phenyl isocyanate. The crystals so obtained are a mixture of the original base, $C_{26}H_{30}N_4$, and the corresponding urea; these were separated by treating with sufficient acetone to dissolve the urea, which is very easily soluble, and leave most of the other body. The acetone solution, on addition of alcohol, gave a crystalline precipitate, which, after dissolving again in acetone and precipitating with alcohol, yielded 0.45 gram of light-yellow diamond-shaped plates. The body, after drying over night in a desiccator, melts at 80°–90° with the evolution of a gas (but no darkening), and by gently heating on a platinum foil gives off much cyanate (recognized by the odor).

A determination of the molecular weight by the freezing-point method in benzene, using 0.43 gram of the substance which had been dried in a vacuum-desiccator over night, gave the value 239 instead of 507, as calculated for the urea, $C_{33}H_{32}N_2O$. The low result indicated a dissociation of the urea into two molecules; but that phenyl isocyanate does not split off in the benzene solution is shown by the fact that the urea was recovered unchanged from the above benzene solu-

tion, after partial evaporation of the solvent, by the addition of alcohol, which, if free cyanate had been present, would have united with it forming a urethane. The additional fact, already mentioned, that a gas was given off on melting at 80°–90°, indicated the presence of some of the solvent, alcohol or acetone, from which the body was crystallized. An experiment seemed to confirm this. A portion of the pure-recovered urea, after drying over night in a vacuum, as before, weighed 0.3664 gram. On keeping in a good vacuum over sulphuric acid, the substance lost weight gradually for a period of ten days, when the weight was 0.3303 gram. The loss amounts to 1.2 molecules of alcohol to one of the urea. The dry urea now melted at 84°–86° without evolution of a gas.

The larger part of the above urea was lost in an attempted analysis in which the tube broke. That the new body was really the urea was shown, however, by heating 0.05 gram, contained in a test-tube, to 120°–130° in a bath; much cyanate was given off, and this was removed by a current of air. After a few minutes, when the odor of the cyanate had entirely disappeared, the residue solidified, at the temperature of the bath, to a yellow crystalline mass; this upon dissolving in a mixture of boiling acetone and alcohol and adding a few drops of water crystallized in the characteristic yellow prisms of the *α*-form of the body $C_{28}H_{20}N_4$. The pure dry crystals so obtained weighed 0.026 gram (theory requires 0.038) and melted at 171°; on cooling, the substance solidified, and on reheating melted at 184°. The above crystals (m. p. 171°) mixed with the pure *α*-form of the body, showed no change of melting-point. The urea is therefore to be represented by one of the following two formulas:



corresponding to the formulas *a* and *b* (p. 136), respectively,

for the body $C_{26}H_{20}N_4$. The ease with which the body decomposes makes it very difficult to carry out any reaction which would discriminate between the two formulas and no solution of the problem has yet been reached.

The β-form of the body, $C_{26}H_{20}N_4$, *does not react with phenyl isocyanate*, except to a very slight extent. The experiment was carried out twice in exactly the same manner, and at the same time as that with the α-form, the same quantity of substance being used. The product treated as before yielded only a very small amount (perhaps 0.05 gram) of a body which was apparently identical with the urea obtained from the α-form, but the larger part, by far, was the unchanged material.

The difference in behavior towards phenyl isocyanate would seem to show that the two forms of the body, $C_{26}H_{20}N_4$, are not identical *in solution*, as would be the case if they were simply physical modifications of the same chemical individual. However, this point cannot yet be considered as settled, and investigation will be continued in this direction.

In conclusion I wish to express my sincere thanks to Dr. Julius Stieglitz, under whose supervision the above investigation has been pursued, for the personal interest he has taken in the work, and for the valuable assistance and instruction received at his hands.

ON THE SOLUBILITY OF ARGENTIC BROMIDE AND CHLORIDE IN SOLUTIONS OF SODIC THIOSULPHATE.

By Theodore William Richards and Henry Burnell Faber.

In the course of a series of experiments having a practical end as their chief aim, several determinations of the solubility of argentic halides in solutions of sodic thiosulphate were made. Since the data concerning this reaction are none too plentiful, it seems worth while to record briefly our incomplete work upon the subject.

The method of procedure was extremely simple. Solutions of sodic thiosulphate of known strength, made by dissolving weighed amounts of pure recrystallized material in water,

were agitated for varying lengths of time in test-tubes at a fixed temperature with an excess of argentic salt. The bromide had been freed from chloride by long continued digestion with potassic bromide, and both argentic halides had been carefully washed, dried, and powdered. At the end of the allotted times, the agitator was stopped, the heavy precipitates were allowed to settle, and two portions were taken from each perfectly clear supernatant liquid by means of an accurate 5.00 cc. pipette. The silver in these portions was now precipitated by sulphuretted hydrogen and collected on a Gooch crucible. Subsequently, the mixed precipitate and asbestos were treated with nitric acid in excess, the nitrous fumes were expelled, and the silver in the mixture was determined by Volhard's method.

The agitator, based upon the apparatus of Noyes,[1] consisted simply of a rotating rod with a number of flat strips of brass soldered at right angles to its axis. The rubber-stoppered test-tubes were strapped to the brass strips by means of rubber bands, and the whole was immersed in a large Ostwald thermostat. A portion of the water of the thermostat was drawn off when it was desired to remove the solutions, so that the mouths of the test-tubes might be uncovered, and of course the projecting mouths were carefully dried. A spring curtain-rod supporter, easily obtained in New England, formed a very convenient support for the rotating rod, when soldered to the sides of the thermostat. The results with the second solution showed that four hours' agitation was enough to insure saturation. No claim of great accuracy is made for the figures; indeed, the variations among them show their crudity; but they more than sufficed for our purpose, and are trustworthy enough to form an adequate basis for the remarks which follow.

[1] Ztschr. phys. Chem., 9, 606; also Schröder: *Ibid.*, 11, 454.

The Solubility of Argentic Bromide in Solutions of Sodic Thiosulphate.

Temperature = 35°.

	Cryst. sodic thiosulphate in liter. Grams.	Weight of silver found in 5.00 cc. solution. Gram.	Time of agitation.	Weight of AgBr corresponding to each gram of thiosulphate. Gram.	AgBr corresponding to $Na_2S_2O_3$. Molecule.
1	100	0.110	4 hours	0.376	0.496
2		0.108			
3		0.106			
4		0.109			
		0.108			
5	200	0.228	4 hours	0.390	0.515
6		0.224			
7		0.225			
8		0.225			
9		0.226	16 hours		
10		0.223			
11		0.220			
12		0.223			
		0.224			
13	300	0.339	4 hours	0.397	0.524
14		0.340			
15		0.347			
16		0.341			
17		0.344			
18		0.337			
19		0.337			
		0.341			
20	500	0.613	4 hours	0.427	0.564
21		0.611			
22		0.611			
23		0.619			
		0.613			

It is thus evident that the quantity of argentic bromide increases more rapidly than the quantity of the thiosulphate. In this respect the behavior of the bromide resembles that of

the chloride, as observed by Stetefeldt[1]. Hence, simply judging from the solubility, one has a right to infer that the solubility concerns itself with the undissociated part of the sodic salt, for this is the part whose proportion increases when the concentration is increased.

The nature of the equilibrium is obviously so complex that the molecular ratios could not be expected to consist of simple whole numbers. Neither could the solubilities of the two halides be expected to conform to one another. In order to test this point, the solubility of argentic chloride in a solution of sodic thiosulphate containing 200 grams of the crystallized salt to the liter was determined. Four parallel analyses of 5.00 cc. of the solution saturated at 35° yielded respectively 0.344, 0.341, 0.342, and 0.341 gram of silver, or on the average, 0.454 gram of argentic chloride per gram of sodic thiosulphate.[2] Thus the molecular ratio was in this case 1 : 0.78 instead of 1 : 0.52 as in the case of the bromide. The difference is undoubtedly due to the different solubilities of the argentic halides in water, which of course must be factors in the complex equilibrium.

It is well known that from these solutions two well-marked double salts[3] (or, more probably, complex salts) may be obtained by crystallization; but of course this fact does not show that these salts exist in the solution. As Barth has pointed out,[4] however, the inability of the solution to give the ordinary reactions of silver shows that a complex ion must be formed. More light might obviously be obtained from observations on the freezing- and boiling-points, as well as of electrolytic conductivities: indeed Barth made an interesting beginning in this direction, and obtained evidence of the existence of a trivalent acid ion in the solution.

We proceeded in a somewhat different manner:—instead of studying the behavior of the pure double salt, we observed

[1] C. A. Stetefeldt. The Lixiviation of Silver Ores: (Craz and Gerlach, Freiberg, Saxony).

[2] Russell found 0.400 and 0.485 by two different methods. The first was evidently not saturated, the second supersaturated. Stetefeldt, p. 19, 20.

[3] Herschel: Edinb. Phil. Jour., **1**, 26 and 398, (1819). Also Lenz: Ann. Chem. (Liebig), **40**, 94 (1841).

[4] Barth: Ztschr. phys. Chem., **9**, 217, (1892).

the change in the freezing-point caused by the addition of argentic bromide to solutions of sodic thiosulphate. In one trial, the addition of 0.8 gram of argentic bromide to 26 grams of a 0.54 mole-solution[1] of sodic thiosulphate *raised* its freezing-point 0.08°, while in another trial the addition of 0.25 gram of argentic bromide to 19 grams of a 0.4 mole-solution raised its freezing-point 0.03°. Further additions in both cases produced no further rise, although much more argentic bromide dissolved; indeed, in the first case a slight fall was subsequently observed.

According to modern hypotheses such a rise in the freezing point can be produced only by the diminution of the number of active particles present. In the present case the addition of another salt with different ions must, as usual, increase rather than diminish the dissociation of the sodic thiosulphate molecule, hence it could have diminished the number of active particles only by causing some of the undissociated material to condense into a complex structure, in which the silver is combined. Thus further evidence of the plausibility of Barth's conclusion as to the existence of a complex ion is afforded. The fact that upon the further addition of argentic bromide, no further rise is produced may be accounted for by the possible concomitant formation of another complex group, containing more silver—a reaction which might involve an increase in the number of active particles. The substances corresponding to these stages may well be the salts $Ag_2S_2O_3.2Na_2S_2O_3.2H_2O$ and $2Ag_2S_2O_3.2Na_2S_2O_3.2H_2O$, which are actually known in the solid state. The double formula is assigned to the second salt, simply in order to show, at a glance, that it contains more silver than the first. It is more likely that this second salt possesses a simpler formula, and that its partial formation, even in the beginning, prevents the rise in the freezing-point from being as great as it would be if influenced by the formation of ions of the first salt alone.

In the course of the work, the depression of the freezing-

[1] That is, a solution containing 0.54×248.3 grams of sodic thiosulphate in a liter. Such a solution would be called by some a 0.54 normal solution; but it seems to us that this nomenclature is an unfortunate one, and that the term "normal solution" should be reserved for the *equivalent* solutions so useful in volumetric analysis.

point of water caused by the addition of sodic thiosulphate was also observed, as follows:

g. mol. in liter.	Depression of freezing-point.
0.202	0.855°
0.404	1.590°
0.535	1.980°

In brief, this paper contains data concerning the solubility of argentic bromide and chloride in solutions of sodic thiosulphate, cognate results upon the freezing-points of the solutions, and a few remarks upon the probable nature of the complex substances formed. The subject is one of great interest, but the time at our disposal, as well as the inherent obscurity of the equilibria of concentrated mixed solutions, does not suffice to present a more complete view of the details of the reaction.

CAMBRIDGE, MASS., NOVEMBER 26, 1898.

NOTE ON THE SPECTRA OF HYDROGEN.

BY THEODORE W. RICHARDS.

In a recent paper B. S. Hutton recounts some interesting experiments, which tend to show that Hasselberg's "white spectrum" of hydrogen really belongs to that substance, and not to impurities[1]. One point he was unable wholly to explain—the fact that Cornu[2] and he always obtained a brilliant red four-line spectrum of hydrogen whenever a trace of oxygen was present. The experience recently gained by Professor Trowbridge and the writer upon this subject furnishes the data for an explanation of the matter, and the object of these few words is to remove the uncertainty[3].

We observed that water vapor under diminished pressure gives the pure red spectrum far more readily than hydrogen itself does, and that when aqueous vapor is mixed with elementary gases it seems usually to be the chosen vehicle for the transport of the electricity. Obviously water must have been formed in Hutton's and Cornu's tubes, and this must have been the source of the red spectrum. The fact that

[1] Hutton: Phil. Mag., September, 1898, p. 338.
[2] Cornu: Journ. de Phys., [2] **5**, 100–103 and 341–354, (1886).
[3] Am. J. Sci., **3**, 117 and 327, or Phil. Mag., [5] **43**, 135 and 349, (1897).

water vapor thus conducts electricity easily may be accounted for by its heterogeneous molecular constitution[1], which is naturally more sensitive to electric stress than the homogeneous structure of the hydrogen molecule. This is only one of the many arguments which go to support the hypothesis that the red spectrum of hydrogen is due to dissociated atoms,—or at any rate to the disturbance caused by the act of dissociation, while the white spectrum is due to a compound structure of polarized particles. Obviously from water only the characteristic lines of atomic hydrogen, not those of molecular hydrogen, could be obtained : and these are obtained so easily that the molecular spectrum of water steps into the background. On the other hand, if the hydrogen is quite dry, as was evidently the case in some of Hutton's as well as in our experiments, the red spectrum requires tremendous heat for its appearance in a state of purity,—a circumstance which hypothesis explains simply by ascribing great stability to the polarized molecular structure of the gas.

Randall has recently published a paper in which he recounts his difficulties in obtaining the pure hot red spectrum of hydrogen free from relics of the cool white one.[2] Strangely enough he speaks of the presence of aqueous vapor as a possible cause of the existence of the white spectrum, when experimentation would have shown him that the absence of water alone makes this spectrum possible in a state of purity. He seems to have overlooked the fact that a large capacity (10,000 electrostatic units, or more according to circumstances) charged with a very high electromotive force—in other words, great current strength—is necessary in order to provide enough heat to yield the hot spectrum from dry hydrogen, even at its tension of least resistance. This tension varies from one-half to one millimeter of mercury, according to the current strength, a value in any case lower than the tensions employed by him (3 to 8 mm.). It is very certain that an ordinary Ruhmkorff coil and Leyden jar, such as those used by Randall, could not yield the red spectrum under

[1] Compare Volterra : Ztschr. phys. Chem., **27**, 375, (1898); also J. Zeleny : Phil. Mag. [5] **46**, 120–154, (1898) etc.

[2] W. W. Randall : This JOURNAL, **19**, 682, (1897).

his circumstances, provided that the gas was dry, as his seems to have been.

It is odd that Randall, while commenting upon a supposed absence of data in our papers concerning the source of our hydrogen, should have himself forgotten to state his mode of generating the gas. His drying train seems to have included sulphuric acid, a dangerous absorbent of water where hydrogen is concerned, but this could not have effected the final result, for the gas whose spectrum he observed had been diffused through platinum. Our hydrogen was prepared by electrolysis from pure dilute hydrochloric acid, was freed from acid by large amounts of potash, and was dried by standing over phosphoric oxide[1]. It is needless to say that we took all the necessary precautions about sweeping out and filling the tubes, so well known to anyone who has had experience in observing the spectra of gases. One regrets that Randall should have fancied a disagreement between his results and ours, when in reality they are wholly concordant.

In the light of all the facts, and the obvious explanation of Cornu's apparent discrepancy, one can hardly doubt that Hutton and others are quite right in ascribing to hydrogen itself, and not to impurity, the "cool" white spectrum of many lines.

CHEMICAL LABORATORY OF HARVARD COLLEGE, DECEMBER 7, 1898.

REPORT.

ON AQUEOUS SOLUTIONS OF METALLIC GOLD, AND ON THE PURPLE OF CASSIUS.

In a recent number of the Annalen der Chemie[2] Richard Zsigmondy has published an interesting account of soluble metallic gold, obtained by reducing gold chloride in very dilute aqueous solution. The following is an abstract of his paper:

Gold can be held in solution in water in different colored conditions. Although the great variety of colors obtained from the colloidal silver of M. Carey Lea cannot be obtained with gold, yet gold solutions are obtained which are deep-red, blue, and black, as well as of shades lying between these col-

[1] Compare Am. J. Sci., **3**, 331; a paper published three months before the date of Randall's. Hutton also overlooked this paper.

[2] Ann. Chem. (Liebig), **301**, 29.

ors, according to the conditions under which the gold is reduced. The blue or violet solutions seem to be the most easily obtained. The red gold solution is the one principally studied. It is obtained by treating very dilute, boiling-hot, and slightly alkaline solutions of gold chloride with different reducing agents, such as formic aldehyde, acetic aldehyde, alcohol, or even hydroxylamine. Many attempts were made, with varying success, but the best conditions are the following: 25 cc. of a solution of chlorauric acid, $AuCl_3.HCl$, containing 0.6 gram to the liter, diluted with 100 to 150 cc. of pure distilled water, and rendered alkaline by the addition of 2 to 4 cc. of a $\frac{2}{10}$-normal solution of potassium carbonate, are heated to boiling. As soon as the liquid begins to boil, it is removed from the flame, and 4 cc. of a solution of 1 part of freshly distilled formic aldehyde in 100 parts of water, is added gradually to the boiling-hot gold solution. In a short time the colorless liquid darkens, becomes light red, and in a few seconds attains a deep-red color, which does not change in the slightest degree on boiling or on standing for months.

If the above directions are not strictly adhered to, not clear red, but darker purple and often violet and blue-black, turbid liquids are formed. The very dilute red solution can be evaporated to half its volume without change, but further boiling will cause it to change to a dark-violet color, and gold will be precipitated as a black powder. The precipitation is probably due to the accumulation of salts which tend to precipitate the dissolved colloidal gold. The solution was purified by dialysis at a temperature of 40° to 50°. The solution can thus be reduced to one-twentieth of its volume in a few days, and solutions containing 0.12 per cent. colloidal gold were obtained, but on further concentration metallic gold was precipitated on the parchment.

The red gold solution passes through the closest filter-paper without change. It is tasteless. On addition of neutral salts, acids, or fixed alkalies, the beautiful red color changes to blue; the liquid becomes turbid, gradually losing its color, and in eight or nine hours the gold all falls to the bottom as a blue-black powder. Potassium ferrocyanide seems to act differently from other salts; it changes the color to green, and after twenty-eight hours to pure yellow, but the gold is not precipitated. Ammonia changes neither the color nor the solubility of the gold. The addition of an excess of alcohol changes the color to dark-violet and precipitates the gold

completely, but the precipitate, at times, retains its solubility in water.

The metallic gold in aqueous solution acts just as most other dissolved colloidal substances when subjected to electrolysis, following the negative electricity to the positive pole, where it is deposited as a black powder, which can readily be recognized as metallic gold when allowed to dry, as it immediately assumes a beautiful golden luster. When a membrane is placed between the electrodes, the gold, like a true colloid, does not pass through the membrane, but is deposited upon it on the negative side.

Mercury does not amalgamate with dissolved gold either on being agitated wlth the solution or on boiling, and even when precipitated with salts amalgamation takes place very slowly and incompletely.

That the dissolved body is really metallic gold and not aurous oxide is shown by analysis of the precipitate caused by sodium chloride. The very small volume of oxygen found is undoubtedly due to air condensed on the surface of the very finely divided precipitate while drying, especially as the equivalent volume of nitrogen was also found.

When we consider the results of analysis together with the fact that gold with metallic luster is deposited on slow evaporation, and further that the reduction was carried out in a boiling-hot solution and by means of a strong reducing agent there can be no doubt that the red solution contains gold in the metallic condition.

The similarity between the colors of these solutions of gold and the colors of thin layers of gold by transmitted light is marked as well as that of red and rose ruby glass. The absorption spectra of the red solution compared with ruby glass, of the blue and violet solution with blue and violet colors of thin layers of metallic gold by transmitted light are almost identical.

In an appendix to his paper the author referred to the fact that Faraday, in a paper on the "Experimental Relation of Gold to Light[1]," described many of these phenomena and actually obtained the red solution of gold but did not recognize it as such, attributing the color to suspended gold in a finely divided condition.

In the same number of the Annalen[2] Zsigmondy has published another article on "The Chemical Nature of the Purple of Cassius," in which the nature of this curious substance seems finally to be cleared up.

There are few substances in the field of inorganic chemistry

[1] Phil. Trans., 1857, 145. [2] Ann. Chem. (Liebig), **301**, 361.

on which so much has been done, and so much written with as little result as this purple of Cassius. Up to the present time there have been two views held as to the chemical nature of this substance; the one that it is a mixture of stannic acid, and metallic gold; and the other, that of Berzelius, that it is substantially a chemical compound of purple gold oxide with the oxides of tin, possibly mixed with an excess of stannic acid.

The solubility of the substance in ammonia favors the latter view, although Schneider lays great stress on its colloidal character and considers the ammoniacal solution as a mixture of the "hydrosols" of gold and stannic acid.

It seemed very likely that the substance is a chemical compound of acid character, and that the solubility in ammonia is due to the formation of a salt, but it was found that by oxidation of stannous chloride, and by allowing very dilute solutions of stannic chloride to stand, the "hydrogel" of stannic acid separated out, which on the addition of a few drops of ammonia liquefied, and so became soluble in water, just as the purple of Cassius does. There can therefore be no salt formation here.

After the solutions of metallic gold in water were obtained, a substance in every way identical with the purple of Cassius was made by mixing colloidal stannic acid with colloidal gold, and precipitating with acids.

The paper is divided into three parts, the first of which is devoted to showing that the substance is not of acid character in its relation to ammonia, and to the preparation of colloidal stannic acids. This part of the work was done with J. Robitschek.

The purple of Cassius was prepared according to the method of Golfier Besseyre,[1] from stannous chloride solution, free from stannic chloride, and gold chloride. The washed and dried preparation was soluble neither in ammonia nor in caustic potash, but when moistened with hydrochloric acid, it was easily soluble in water. When fresh and moist it is insoluble in concentrated ammonia, potassium hydroxide, or potassium carbonate, but dissolves on dilution. The ammonia solution can be boiled if left dilute so that no odor of ammonia can be detected even on addition of caustic potash, and only a trace can be detected by titration, without precipitating the substance. That the solubility in ammonia or potassium hydroxide is not due to the formation of a salt is also shown by the small percentage of these substances found on analysis —0.003 ammonia in 1 gram and 0.4 cc. normal alkali in 1

[1] Ann. chim. phys., **54**, 40.

gram. The solubility in these reagents seems to be due to the liquefying property of the alkalies. The purple of Cassius behaves in every way like a colloid substance toward the electric current and porous membranes.

By passing a strong current of air through a very dilute solution of stannous chloride, free from gold, and allowing it to stand, it was oxidized gradually to a colloid stannic acid, which is precipitated, and, when washed free from chlorine, behaves toward reagents neither like ortho- nor meta-stannic acid. It is insoluble in strong hydrochloric acid, nitric acid, or caustic potash, but dissolves immediately on diluting to double the volume. It is soluble in water after moistening with ammonia. We have here the "hydrogel" of stannic acid which behaves toward the electric current like the purple of Cassius.

A colloidal stannic acid can also be obtained from stannic chloride when a very dilute solution of the latter (2 grams in 3 liters) is allowed to stand for several hours. A voluminous precipitate comes down which, when washed free from chlorine, moistened with a few drops of ammonia, and diluted, dissolves to a clear liquid which can be boiled without precipitation of stannic acid. This preparation differs from the former in that it is soluble in strong or dilute hydrochloric acid, and potassium hydroxide, and not entirely in nitric acid. Potassium carbonate precipitates it from its hydrochloric acid solution but does not dissolve it in excess.

From their properties these forms of stannic acid are seen to be neither ortho- nor meta-stannic acid, but they can be looked upon as colloidal mixtures of the two rather than individuals lying between the two, the properties of the one being hidden by those of the other. The purple of Cassius is such a mixture of gold and stannic acid hydrate, in which the stannic acid imparts to the metallic gold the property of dissolving in water by means of alkalies. This is the reason why so many chemists have for so long a time considered the substance to be a chemical compound. By mixing a solution of either of these colloidal stannic acids with a solution of colloidal gold, and precipitating by means of dilute acids or salt solutions, a gold-purple can be obtained of any desired composition and intensity of color, in fact any of a great variety of shades. The mixture does not turn blue and then precipitate gold when treated with acids or salts, like the red gold solution, but remains unchanged even on long standing, but when boiled a red body is precipitated which behaves, in every respect, like the purple of Cassius.

The formation of the purple of Cassius is explained by

assuming that when stannous chloride is added to a sufficiently dilute solution of gold chloride, the latter is immediately reduced to metallic gold, while stannic chloride is formed. Generally after a few seconds the liquid becomes red, but the purple is not precipitated for several days unless it is heated. The gold is not precipitated as a black powder because the stannic chloride formed is immediately hydrolyzed into hydrochloric acid and the hydrate of stannic acid. The latter prevents the aggregation of the gold particles, and the stannic acid remains in solution as a colloid which on standing gradually changes under the influence of the dilute hydrochloric acid to an insoluble form, the "hydrogel" of stannic acid. By heating, this change takes place immediately.

The properties of purple of Cassius depend on the properties and character of the stannic acid present, the gold playing a passive rôle in its relation to reagents. If the stannic acid is soluble in concentrated hydrochloric acid, so is the purple, but if it has the properties of metastannic acid, it is insoluble in that reagent but dissolves on distillation. In the same way the solubility in ammonia or dilute alkalies depends upon the character of the stannic acid present; in fact the great variety in the properties of the stannic acids explains the many contradictions in the literature with reference to the properties of the purple of Cassius. Zsigmondy says, "I look upon the knowledge that a mixture of colloid bodies can behave under some conditions as a chemical compound, and that the properties of one body in such mixtures can be hidden by those of another, as the most important conclusion to be drawn from this work."

By mixing the "hydrogels" of stannic acid and silver and precipitating with dilute sulphuric acid, a red-yellow body was obtained, which is soluble in ammonia, and a similar body was also obtained by reducing silver nitrate in the presence of a stannic acid solution. C. L. REESE.

REVIEWS.

TRAITÉ D' ANALYSE DES SUBSTANCES MINÉRALES. Par ADOLPHE CARNOT. Tome premier; Méthodes générales d' Analyse qualitative et quantitative. Paris. V^ve^ Ch. Dunod. 1898. 992 pp.

This, the first of three volumes, gives promise of one of the most extensive and important works on inorganic analysis which have appeared for very many years, and well fulfils the promise as far as general methods are concerned, leaving to the remaining two volumes, soon to be completed, the detailed and special methods applicable to particular classes of material. The whole work is to contain about 3000 pages.

In the volume already published the first chapter is devoted to the use of the blowpipe, the second to Bunsen's flame reactions, and the third to the spectroscope, this last giving much fuller information as to the use of the instrument, particularly with the aid of high temperature electric sparks, than is found in most of the common manuals of chemical analysis. In the fourth chapter much useful information as to characteristic reactions observable under the microscope—so-called microchemistry—has been brought together from sundry separate works and individual memoirs. The fifth chapter takes up the means of getting into solution substances to be examined, and the group reactions in the liquid way of the solutions obtained; in this the rare elements, such as thallium, germanium, indium, and thorium, are treated of on the same footing as the most common. The sixth chapter is devoted to the individual reactions of the several basic and acid radicals, given in much detail—thus, under manganese we have separate consideration of manganous and manganic salts, of manganates and permanganates, and under sulphur we have sulphates, sulphites, thiosulphates, sulphides, hydrosulphites, di-, tri-, tetra-, and pentathionates. Chapter VII discusses reagents, gives directions for obtaining these in a pure state, including such substances as hydrogen and oxygen gases, and takes notice of some recently introduced or less common reagents, such as sodium dioxide, ammonium formate, calcium thiosulphate, and bismuth chloride. In chapter VIII quantitative analysis is begun, and the selection and purification of samples, pulverization, desiccation (under various conditions), and weighing are considered. Chapter IX contains the details of operations in the dry way at high temperatures, with good descriptions of furnaces (for solid and gaseous fuel), crucibles, etc., and useful information as to calcination, fusion, etc., which reflects in part the experience of the author as professor of assaying in the *École des mines* at Paris. In Chapter X we have a discussion of the chief apparatus and processes used in operations in the liquid way—solution, evaporation, distillation, filtration, etc. Chapter XI is devoted to modern electrolytic apparatus and methods, of which a clear general account is given, including the measurement of currents—special applications of electrolysis are reserved for the succeeding volumes. Volumetric methods, the measuring vessels, choice and preparation of standard solutions, indicators, etc., are treated of in Chapter XII—individual determinations are left over to the later volumes. In Chapter XIII there is a rather brief account of colorimetric methods, less full and satisfactory, perhaps, than any other part of the

book. The fourteenth and last chapter is taken up with the means of analyzing gaseous mixtures, the collection of samples of gas from mineral springs, the soil, furnaces, chimneys, and other sources, and the apparatus and processes of gas analysis, with notice of the methods for detecting and quantitatively determining fire-damp in the atmosphere of coal mines.

The large volume is well printed, and well illustrated, and amply deserves a place on the book shelves of every well-equipped laboratory. J. W. M.

OUTLINES OF INDUSTRIAL CHEMISTRY. By FRANK HALL THORP, Ph.D., Instructor in Industrial Chemistry in the Massachusetts Institute of Technology. New York. The Macmillan Company. 1898. xvii +541 pp.

This book is intended, as the author says in his preface, to furnish an elementary course for students in Industrial Chemistry, which may serve as the groundwork for a more extended course of lectures, if desired. It seems to carry out this purpose in a way likely to be useful.

In the treatment of so extensive a subject scarcely any two teachers, perhaps, would agree exactly as to what should be included and what omitted, or as to the relative amount of space to be devoted to the various subdivisions of the work. Metallurgy is altogether left out, as representing an independent branch of study, and the whole subject of artificial dye-stuffs is treated in nine pages. Some may be inclined to think that at least a little space might have been given to such matters as bread-making, milk and its manufactured products, artificial stone, the preservation of timber, and the new industry of synthetically made materials for use in perfumery. And perhaps enumeration of the different inks now in use might more advantageously have taken the place of mention given to such materials as assafœtida, euphorbium, myrrh, and Iceland moss. But on the whole the distribution of matter is good, and the condensation has been judiciously effected.

The point which seems to the writer of this notice most open to criticism is meagreness in the description, and lack of the necessary wood-cuts, to render intelligible machinery and appliances for the actual conduct of several important processes, such as the manufacture of gunpowder, calico-printing, etc. Nothing should more markedly distinguish the teaching of industrial from that of general or scientific chemistry than a clear discussion, not only of what result is aimed at in each manufacturing process, but further of just *how* such result is practically reached with most economy of material, labor, and time. In this direction the author of the book un-

der review has done well to begin with a chapter on some of the most common and variously applied processes, such as lixiviation, evaporation, etc. But this chapter might well have been expanded, so as to include, for instance, a notice of *systematic* leaching in order to separate soluble from insoluble material with maximum completeness and minimum quantity of the solvent, and a fuller explanation of the purification of substances by crystallization from solution, washing of the crystals, disposal of mother-liquors, etc. More than merely incidental reference might well have been made to the electric furnace and its increasing use, and to the growing extension of electrolytic processes. It is always desirable to draw the attention of students to analogous or competing methods of reaching the same ends, and to present clearly the advantages and drawbacks which severally belong to them—thus, for example, it is very instructive to contrast fully the Leblanc with the Solvay process for making carbonate of soda, and the conditions under which gunpowder and the modern "high explosives" may respectively replace each other with advantage in use. Such comparisons are not altogether neglected in this book, but they might perhaps have been made more prominent. A very good feature of the work is the list, given at the end of each chapter, of references to more extended works, papers in scientific journals, etc., where the student may find fuller details when desiring to go further into the subject and to specialize his knowledge of it.

The general impression made by the book is decidedly favorable, and it is to be hoped that it may meet with such success as to cause a demand for other editions, in which it may be rounded out by improvement in some details, and may become a standard text-book. There has been much need for such a work in English, v. Wagner's well-known *Handbuch der chemischen Technologie* being deformed by absurd blunders of translation—such as the confusion of geographical degrees of latitude with degrees of the thermometric scale!—blunders which have been perpetrated in an earlier and perpetuated in the last edition. J. W. M.

A Short Manual of Analytical Chemistry, Qualitative and Quantitative—Inorganic and Organic. By John Muter. 2d American, adapted from the 8th British edition. Philadelphia: P. Blakiston's Son & Co. 1898. xiii+228 pp.

This manual proposes to give a concise course of instruction in chemical analysis, qualitative, quantitative, and in special applications, primarily and chiefly for students of pharmacy. The condensation of matter is certainly remarkable, and its selection has no doubt been on the whole judiciously made in

the interest of those for whom the book is intended. They will find much information of a practically useful sort in such chapters as that on the detection of alkaloids (including some of the less familiar members of this class, as narceine, physostigmine, pilocarpine, etc., and with them some substances not alkaloidal in character, but liable to be confounded with alkaloids, as acetanilid and antipyrin), that on the detection of some miscellaneous organic substances interesting in connection with medicine or pharmacy—*e. g.*, benzine (petroleum spirit), and benzene from coal-tar, beech-tar creosote, paraldehyde, naphthol, resorcin, phenacetin, sulphonal, etc.,—that on the analytical examination of important drugs (assay of opium and of cinchona bark, detection of "methylated spirit" in tinctures, etc., examination of fixed oils and fats, of soaps, and of so-called essential oils, etc.).

But it may well be doubted whether condensation has not been carried too far. The book is manifestly intended for practical use in the laboratory, and one cannot but hesitate as to the safety with which important investigations may be based on such instructions as can be given within some of the limits observed. Thus, the "general sketch of the method of testing for poisons in mixtures" takes up less than a page and a half, the individual reactions, it is true, being given elsewhere. The use of the polariscope is disposed of in two pages, and spectrum analysis in little more than a single page.

While a very large amount of information has been included, there are here and there noticeable omissions of statements that one might naturally expect to find. For example, in describing the reactions of cobalt no mention is made of the well-known yellow cobalt-potassium nitrite, and for the detection of nitrites no reference is made to the Griess reaction with sulphanilic acid and a salt of naphthylamine. Neither in the description of the reactions of arsenic nor in the chapter on poisons is any hint given, in connection with Marsh's and Reinsch's tests, of the need for care as to the freedom from arsenic of the reagents used.

The book is to some extent marred by occasional loose forms of expression, a defect which is much to be deprecated when the mental interests of students are considered. Thus, on p. 1, "Solution" is defined in these words—"This process consists in leaving a *solid* body in contact with a fluid until it dissolves, heat being occasionally used." Aside from the objection to defining the noun by the same word in the form of a verb, there is here no recognition of solution affecting a gas or a second liquid. Again, on p. 2, "Precipitation" is defined—"This process consists in mixing the solutions of two

substances *so as to form a third substance*, which, being insoluble in the fluids employed, sinks to the bottom." The common pharmaceutical process of precipitating an alcoholic solution of camphor by addition of water does not involve the formation of a third substance. On p. 5, the expression is used—"A *peculiar kind of fusion*, called cupellation, is resorted to in the assay of gold and silver bullion." This is hardly a satisfactory definition of cupellation. On the same page, in explaining what is meant by crystallization, it is stated that "Many substances when dissolved in a boiling liquid separate out, *as soon as the fluid cools*, in masses having a well-defined and symmetrical shape." This does not apply to the case of common salt crystallized by evaporation of water from continuously heated brine, and a beginner without experience might easily derive the idea that when a heated (why boiling ?) solution cools the *whole* of the dissolved solid separates in crystallized form. There is no mention of substances like iodine or benzoic acid, crystallized on condensation of the vapor. On p. 96, in illustration of the mode of using the hydrometer it is said—"Suppose an elongated body with a weight at its base to cause it to float upright, which has a specific weight exactly half that of water, be immersed in that fluid, it will sink to exactly half *its length*." This certainly is not true of a hydrometer of the usual form, such as is shown by a wood-cut on the next page, nor is it true even of a cylinder or prism of uniform cross-section having "a weight at its base." On page 100 we have the following decidedly unscientific problem and general solution thereof —"To find the amount of solid matter" (No particular kind of matter is referred to, nor is the solvent specified; presumably water is meant), "in grammes, present in 100 cc. of a solution of a given specific gravity. So far as any ordinary rule" (What is an ordinary rule ?) "can be laid down, especially with regard to saccharine liquids, for which this calculation is generally used, we multiply the gravity by 1000, and then, having deducted 1000 from the product, we divide by 3.85." On p. 104—"Volumetric or standard solution is a solution of definite strength, made by dissolving a given weight of a reagent in grams in a definite volume *of water* in cubic centimeters." In all the standard solutions commonly used in volumetric analysis, such as are referred to in the following pages, the "definite volume" required is not that of the water, but of the solution. In quoting these examples, italics, not those of the author, have been made to indicate the words unfortunately used.

J. W. M.